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Faculty of Engineering – Department of Civil Engineering

COLD MIX ASPHALT MADE WITH BITUMEN EMULSION CAPSULES

By

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"Every successful person has a painful story.

Every painful story has a successful ending.

Accept the pain and get ready for success."

-Unknown

Abstract

Numerous studies have identified the benefits of cold mix asphalt (CMA) made of bitumen emulsion, compared to hot mix asphalt (HMA) made with bitumen. When CMA made with bitumen emulsion is used, more than 95% of the energy can be saved during its production. Also, heating is not required while mixing and compacting the CMA. However, emulsion mixes are used in the United Kingdom mainly for surface treatments due to weak early life strength, high air voids and long curing times.

This present study investigates the performance of cold mix asphalt made with bitumen emulsion capsules. The initial objective of the research is to produce bitumen emulsion capsules with minimum water content, then mix the aggregates and bitumen emulsion capsules, followed by compaction at ambient temperature to provide enhanced mechanical properties as compared to conventional CMA made of bitumen emulsion. The bitumen emulsion capsules were produced by bitumen emulsion droplets coated by a shell made with calcium-alginate (Ca-alginate). Then the bitumen emulsion capsules were mixed with aggregates and compacted at ambient temperature. The research was undertaken to evaluate the effect of compaction energy, different cement contents, curing times and binder types on the mechanical properties of cold mix asphalt made with bitumen emulsion capsules. This research revealed that the mechanical properties of cold mix asphalt made with bitumen emulsion capsules increase with the increase of compaction energy. Moreover, the mechanical properties of cold mix asphalt made with bitumen emulsion capsules increased with curing time. The study also revealed that Ca-alginate was, itself, an effective binder type that can hold aggregates together resulting in better mechanical properties of mixtures. Thus, it was concluded that a cold mix pavement material made with Ca-alginate binder is a novel material for pavements with potential to be an alternative for conventional cold mix asphalt made with bitumen emulsion.

Dedication

This thesis is dedicated to

My wife and child …

My parents, brothers and sister…

Thamer Alenezi,

Acknowledgements

I would like to thank my supervisors, **Dr. Alvaro Garcia Hernandez** and **Mr. Andrew Dawson**, for their guidance and supervision during my PhD studies.

I would also like to thank **Dr. Nick Thom** on his observations and recommendations during the first and second viva of my research.

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I wish to extend my thanks to Jon Watson, Richard Blakemore, Martyn Barret, Lawrence Pont, Mathew Thomas, Laura Weatherby and Antony Beska for their help with the experiments.

Finally, I must express my heartfelt gratitude to all the distinguished individuals who in one way or another assisted me during my PhD studies.

Thamer,

July, 2018

Declaration

The research was conducted at the Nottingham Transportation Engineering Centre of the University of Nottingham. I hereby declare that this dissertation is my own work and has not been submitted for a degree of another university.

Thamer Alenezi,
July, 2018
University of Nottingham

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Chapter 1: Introduction

1.1 Background and Problem Statement

Cold mix asphalt (CMA) is one of the most studied types of asphalt emulsion mixes. The main advantage of CMA is that it can save up to 95% of the energy compared to traditional hot mix asphalt (HMA) (Chappat and Bilal, 2003; Chehovits and Galehouse, 2010). There are a variety of ways in which CMA can be produced and this includes using 100% virgin aggregates or utilising RAP. However, previous studies indicate that the application of CMA is still facing many challenges, some of which are associated with the lack of commonly accepted mix design techniques (Lee et al., 2002; Thanaya et al., 2009; Diefenderfer et al., 2012; Stroup-Gardiner, 2012). The lack of consensus is attributed to a number of reasons that include weak early life strength, high air-void, and the long curing times associated with CMA (Ojum, 2015). Accordingly, use of CMA is limited in the United Kingdom largely to surface treatments, such as surface dressing and slurry surfacing, as well as bond/tack coating (Brown and Needham, 2000). In fact, the curing duration and the moisture content have a huge effect on the CMA properties (Mamlouk, 1979; Kim and Lee, 2010; Wirtgen, 2004). Consequently, previous researchers have used additives such as Ordinary Portland cement (Terrell and Wang, 1971; Schmidt et al., 1973; Head, 1974; Needham, 1996; Thanaya, 2003; Oruc et al., 2007; Niazi and Jalili, 2009; García et al., 2013; Fang et al., 2016; Nassar et al., 2016), rapid hardening cement (Thanaya, 2003; Fang et al., 2016), and fibres (Bueno et al., 2003, Ferrotti et al., 2014) to address the long-term performance of CMA and compared it to traditional hot mix asphalt. However, most of the previous attempts failed to deliver the required performance. This research proposes a new approach in which a type of capsule, containing bitumen emulsion, is used in cold mix pavement material. The aim is to improve the strength and reduce the curing time by delivering the binder more uniformly throughout the mix than is achieved by other cold-mix approaches.

1.2 Aim and Objectives

1.2.1 Aim

The aim of this research is to investigate the performance of cold mix asphalt made with bitumen emulsion capsules.

1.2.2 Objectives

The main objectives of this research are as follows:

1. Evaluation of the morphology and composition of the capsules and particles.
2. Evaluate the effect of binder type and amount on the mechanical strength of capsule-based cold mixes at different curing times.
3. Evaluate the effect of (in various combinations): compaction energy, Portland cement addition, rapid hardening cement addition, curing times and water content on Marshall strength of CMA mixtures made with Ca-alginate capsules containing bitumen emulsion.
4. Compare the strengths of the capsule-based mixtures with HMA mixtures.
5. Investigate the use of Ca-alginate capsules containing no bitumen emulsion.

1.3 Thesis Structure and Outline

- **Chapter One: Introduction**

This introduction describes the background of CMA and the motivation of the research topic. In addition, the problem statement, aim, objectives and thesis outline of this research are included in this chapter.

- **Chapter Two: Literature Review**

This chapter provides an overview of asphalt pavements and the types of asphaltic

materials for road pavements. The main focus in the literature review is on the background of CMA. Also, this chapter reviews the encapsulation techniques as well as assessing physical characteristics and chemical composition of capsules. Furthermore, this chapter reviews the alginate as an encapsulation material with its chemical and physical properties as well as the variants of alginate.

- **Chapter Three: Cold Mix Pavement Material made with Calcium-Alginate and Aggregates**

This chapter presents the size distribution, and morphology of the capsule production, and the mechanical strength of test specimens made with Ca-alginate capsules. This chapter details the effect of cement addition and compaction energy on the mechanical strength of cold mix pavement materials made with Ca-alginate capsules (CMC). This chapter also presents the effect of binder type used, i.e., bitumen emulsion, Ca-alginate capsules or particles and amount on the mechanical strength of cold mixes at different curing times.

- **Chapter Four: Cold Mix made with Calcium-alginate Capsules that Contain Bitumen Emulsion and Rapid hardening Cement**

This chapter presents the effect of fast-curing cement on the mechanical strength of CMC. In particular, the focus is on the mechanical strength due to the use of rapid hardening cements and this is compared to the effect of Portland cement in CMC.

- **Chapter Five: Moisture Resistance of Cold Mix made with cement-treated Calcium-alginate Capsules that Contain Bitumen Emulsion**

This chapter presents the mechanical properties of CMC. The main focus is on the mechanical properties of CMC materials, with and without cement, with regard to curing time and moisture content.

- **Chapter Six: Overall Discussions**

This chapter describes the main findings from this research. The main focus is on the

mechanical properties of CMC materials, with 1% of cement, both dry and wet condition, comparing to that of HMA.

- **Chapter Seven: Conclusions and Recommendations**

This chapter contains the main conclusions and recommendations based on the findings of the study.

1.4 Publication List

❖ **Conference paper:**

Alenezi, T., Garcia, A and Norambuena-Contreras, J., 2018. Mechanical performance of cold mix asphalt with bitumen microcapsules. (Accepted and presented as conference paper)

❖ **Journal paper:**

Alenezi, T., Norambuena-Contreras, J., Dawson, A and Garcia, A., 2019. A novel type of cold mix pavement material made with calcium-alginate and aggregates. (Article published in Journal of Cleaner Production)

Chapter 2: Literature Review

2.1 Asphalt Pavement

Asphalt pavements are a combination of bitumen and aggregate materials, constructed of different types and in different thicknesses (Martin and Wallace, 1958). Basically, asphalt pavements are widely recognised as flexible pavements consisting of a multi-layer system, which overlies the subgrade (as shown in Figure 2.1). The subgrade as mentioned by Mathew and Krishna Rao (2007), is a natural soil layer that must accommodate the stresses from the layers situated above. However, when the subgrade layer is weak, it is imperative to have a capping layer above it, such as hydraulically bound material (Thom, 2008), to achieve certain strength properties required for the type of pavement being constructed (Garber and Hoel, 2014). The sub-base is the lowest pavement layer and is covered by a base course, as well as wearing course, usually bound with bitumen binder (Yoder and Witczak, 1975; Brockenbrough and Boedecker, 2003). Therefore, a flexible pavement design, as outlined by Martin and Wallace (1958), is rooted in the principle that a load of any magnitude can be dissipated by conveying it deep into the ground by means of successive layers.

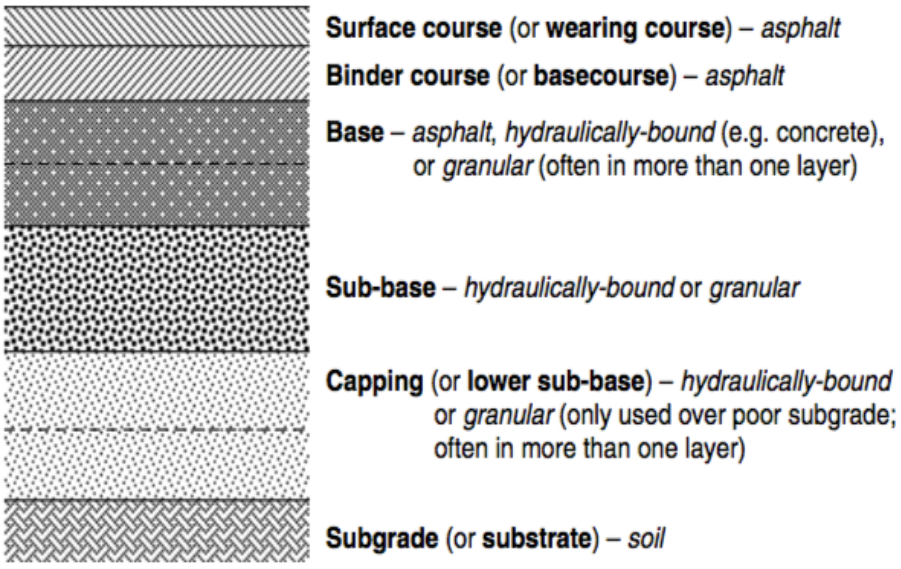

Figure 2.1 Layers in a typical flexible pavement (Thom, 2008).

As observed in Figure 2.2, the level of stress induced in overlying layers is dependent on the elastic stiffness underneath each layer. Hunter (1994) reported that the essential pavement design criteria are based on the interaction between the elastic stiffness of the base, the shear stress in the foundation and the tensile stress in the road base. However, Yoder (1975) argued that even though a pavement material with higher stiffness can reduce the risks associated with a subgrade layer, such as shear, the presence of this stiff layer increases the tensile stress underneath of this layer and increases horizontal shearing stress. Therefore, the shear and flexural resistance of this stiff layer must be high enough to sustain high stress conditions.

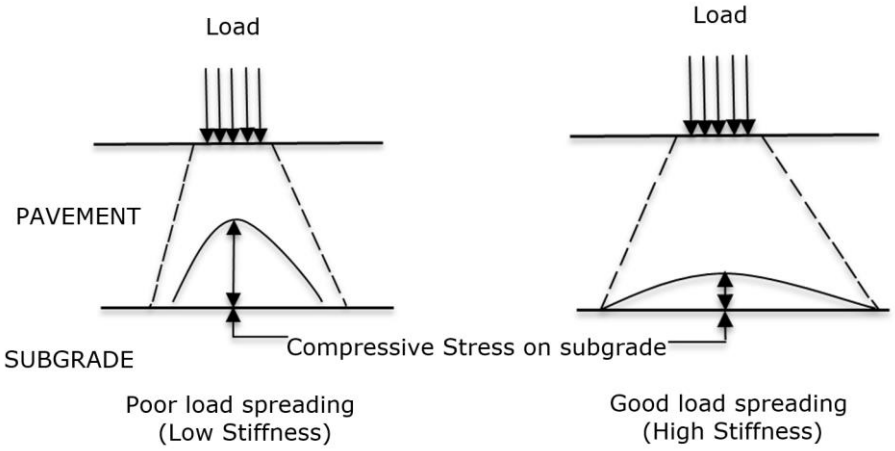

Figure 2.2 Pavement stiffness and load spreading through asphalt layers (Brown, 1988).

2.2 Types of Asphaltic Materials for Roads

Road pavements normally consist of specified mineral aggregates bound by bituminous material. These blends of aggregate and bitumen can be classified into four types: Hot Mix Asphalt, Warm Mix Asphalt, Half-Warm Mix Asphalt and Cold Mix Asphalt (EAPA, 2010). The main differences between these types are the production and compaction temperatures, as discussed in the following sections.

2.2.1 Hot Mix Asphalt (HMA)

HMA is a bituminous mixture produced and compacted at elevated temperatures, generally between 110-180°C. Due to the high temperatures required to produce HMA, a lot of fuel is needed to heat the bitumen and the aggregates. Recent surveys conducted by Skolnik et al. (2013) and Sullivan and Moss (2014) have established that 275 MJ of energy is consumed in producing 1 tonne of HMA, which constitutes up to 15% of the total cost of manufacturing HMA (Chappat and Bilal, 2003; Chehovits and Galehouse, 2010; Sullivan and Moss, 2014).

2.2.2 Warm Mix Asphalt (WMA)

The WMA production temperature typically ranges between 120°C and 130°C and, according to D'Angelo et al. (2008), this asphalt is believed to be a favourable substitute for HMA. The strength and durability of WMA are comparable to that of HMA. However, the difference between WMA and HMA is the lower temperature required to achieve suitable workability. There is also a limited 20-35% burner fuel saving attributed to WMA compared to HMA.

The production process involves adding additives and binding materials to reduce the viscosity of bitumen at medium temperature; these include zeolites, emulsions and wax to facilitate mixing and compaction. Additionally, WMA is considered beneficial because it produces less smoke, fumes, and dust, since the placing and spreading processes occur at lower temperatures.

2.2.3 Half Warm Mix Asphalt (HWMA)

Researchers in the asphalt industry are continually searching for ways of making the process more environment friendly, reducing the consumption of energy, and ensuring that it is cost effective. Punith et al. (2013) comment that, in practice, the asphalt mixing temperatures using WMA could be reduced to temperatures between 120°C and 130°C, but using HWMA, temperatures could be reduced to below 100°C. After heating, they are

mixed and spread at temperatures between 80°C and 90°C. Because temperature remains below 100°C, the aggregates in HWMA have a substantial amount of moisture.

2.2.4 Cold Mix Asphalt (CMA)

When CMA is used, more than 95% of the energy required during the production of HMA can be saved (Chappat and Bilal, 2003; Chehovits and Galehouse, 2010), see Figure 2.3.

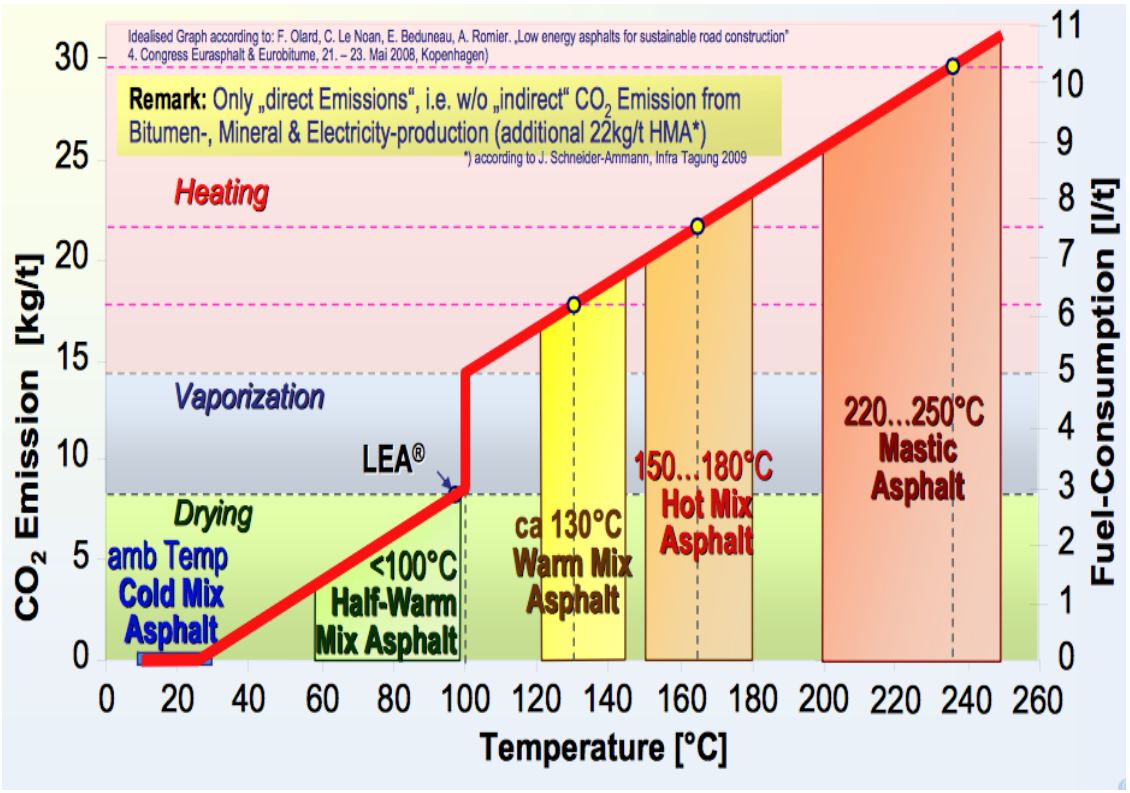

Figure 2.3 The CO² emissions and energy consumption (Partl, 2010).

An extensive literature review has revealed numerous types of cold mixtures such as:

- Cold Lay Macadam

Cold lay macadams (CLM) are mixtures of low viscosity bitumen and aggregates formed through the addition of flux oil or solvent into the bitumen (cutback bitumen). Flux oil is a moderately non-volatile part of petroleum used as a dilutent for softening bitumen to the required consistency. Nickolls (1998) asserts that there are different types of flux oil: kerosene, white spirit, creosotes, gas oil, and a combination of these. Cold lay macadams

have been used for surface dressings, surface macadam and for filling temporary reinstatement work. Robinson (1997) pointed out that such mixtures have revealed low stiffness because of the flux oil.

- Foamed Bitumen

Foamed bitumen was first described in 1956 by Iowa State University professor Ladis H. Csanyi (Csanyi, 1957). Csanyi created the foamed bitumen through injection of water- into hot bitumen causing a steam-generated foam with a lot of tiny bitumen covered bubbles. The process of foaming lasts for less than one minute before dissipating, whereupon the original characteristics of bitumen are regained. Therefore, mixing with aggregates can be achieved while the binder is still in the foamed state (see Figure 2.4). However, Kendall et al. (2000) found that this process is not suitable for every type of pavement. Moreover, the process needs hot bitumen at a temperature of 180^0C so that the foaming action is successful, but this means the risk of heating is high.

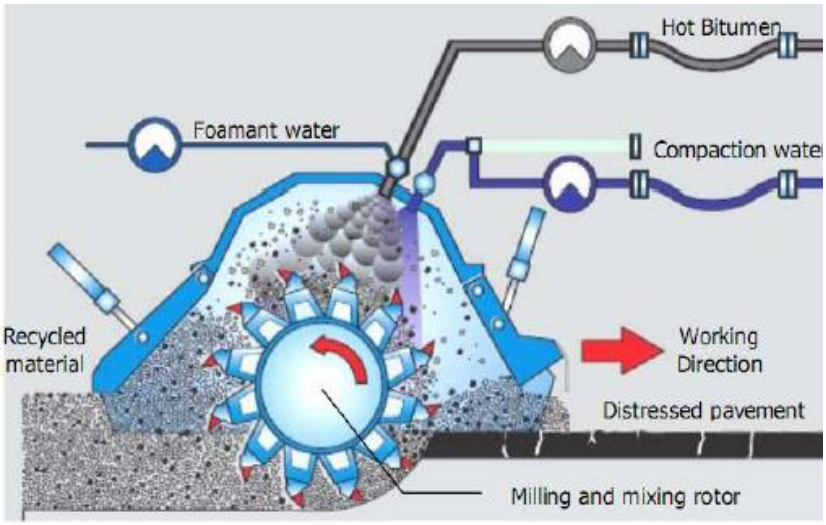

Figure 2.4 Foamed Asphalt application for cold pavement recycling (Ebels et al., 2005).

- Cold bitumen emulsion Mixture (CBEM)

CBEM is predominantly made up of graded mineral aggregates as well as bitumen held in a water emulsion. This can be mixed and compacted at ambient temperature without the need for heating (Thanaya, 2003). The use of bitumen emulsion in the United Kingdom is

largely limited to different types of surface treatment (like surface dressing and slurry surfacing) as well as bond/track coating (Brown and Needham, 2000). After compaction the emulsion 'breaks' and the water leaves the mix (by drainage evaporation or consumption by the hydration process of adjacent cement) leaving a bitumen-bound aggregate (i.e. asphalt).

2.3 Advantages and Disadvantages of CMA

As reported in a number of studies such as Needham (1996), Thanaya (2003), James et al. (1996), and Choudhary et al. (2012), CMA has many advantages, including a reduced carbon footprint in the processes of production, lower than every other bituminous mixture. There is also no need to dry the aggregates to be used in emulsion or foam mixtures, and no dust is emitted. Moreover, the total amount of energy required during the production process is less, since heat is only required during bitumen emulsion or foam production, and not during compaction and mixing.

On the other hand, Thanaya et al (2009) stated that there are some disadvantages in the utilisation of CMA, as summarised below:

- High air-void content of the compacted mixtures.
- Weak early life strength (caused by the poor adhesion between cold bitumen and aggregates).
- Long curing times (evaporation of water/volatiles content and setting of the emulsion) required to achieve maximum performance.

Nevertheless, cold mix asphalts (CMA) made with bitumen emulsion are adopted in this research because they are eco-friendly, cost effective, and safe to handle and mix.

2.4 Materials for CMA

The general contents of CMA include bitumen emulsion (which acts as a binder) as well as aggregates prepared at ambient temperature. The following subsections will provide a brief overview of CMA (including the bitumen emulsion, classification of emulsions, stabilisation theory of bitumen emulsions, aggregate gradation and type).

2.4.1 Bitumen Emulsion

An emulsion can be defined as the dispersion of a liquid's fine droplets into another liquid (Needham, 1996). With regard to bitumen emulsions, they are two-phase systems that contain two immiscible liquids (water and bitumen), which are normally stabilised by the emulsifier (Shell Bitumen, 1995). Bitumen emulsions usually consist of 40-75% bitumen, 0.1% to 2.5% emulsifier, and 25% to 60% water (Salomon, 2006).

2.4.2 Classification of Emulsion

The classification of bitumen emulsion is based on the surface charge of the dispersion phase, emulsification technique and the droplet size.

As stated by Read and Whiteoak (2003), the surface charge of bitumen emulsions can be classified into four types: cationic, anionic, non-ionic and clay-stabilised emulsions. The cationic and anionic are the most frequently used emulsions. Cationic emulsions are basically acid emulsions having a pH lower than 7 as well as a positive electrical charge, whereas anionic emulsions are normally alkaline, having a pH value higher than 7 as well as a negative electrical charge (Thanaya, 2003). The typical cationic and anionic emulsion recipes are shown in Table 2.1. Rapid-setting (RS) emulsions are those which normally set rapidly after coming into contact with a clean, low-surface area aggregate, like the chippings utilised in chip seals (surface dressings); while slow-setting (SS) emulsions are those that mix with high-surface area reactive aggregates. However, the most commonly used bitumen emulsions are cationic bitumen emulsions, because they usually lead to favorable interfacial electrostatic interactions, and also can be modified in numerous ways

to meet nearly all requirements (Boulangé and Sterczynskia, 2012; Suleiman, 2006). Figure 2.5 shows a schematic diagram of bitumen during dispersion in an emulsifier.

Table 2.1 Typical emulsion recipes in % (Salomon, 2006).

Cationic RS		**Cationic SS**		**Anionic RS**		**Anionic SS**	
Asphalt	65	Asphalt	60	Asphalt	65	Asphalt	60
Tallowdiamine	0.2	Tallow Diquaternary Ammonium Chloride	0.6	Tall Oil	0.3	Ethoxylated Nonyl phenol	0.5
Hydrochloric Acid, 35%	0.15			Sodium Hydroxide	0.2	Lignins	0.5
Soap pH	1.5-2.5	Soap pH	3-7	Soap pH	11-12	Soap pH	10-12
Water	to 100	Water	to 100	Water	to 100	Water	to 100

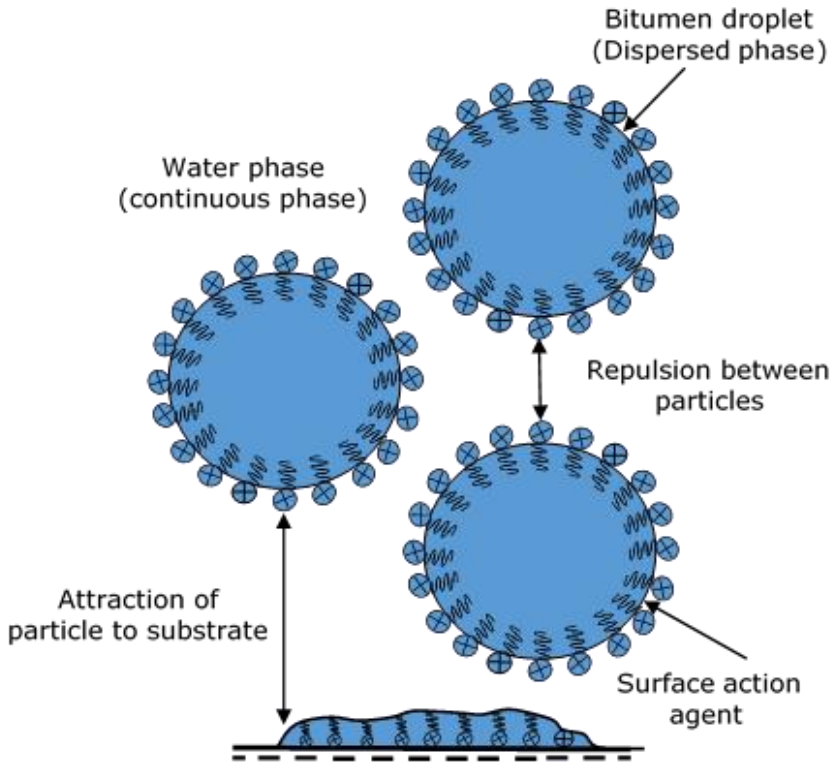

Figure 2.5 Schematic diagram of bitumen during dispersion in an emulsifier (Read and Whiteoak, 2003).

As stated by Gibb (1996), the emulsifier in bitumen emulsion reduces the interfacial tension between water and bitumen. The emulsifier acts as a stabiliser in the emulsion

and supports the adhesion between the mineral aggregates and bitumen. Typically, an emulsifier has lipophilic or hydrophobic as well as oleophobic or hydrophilic portions (Thanaya, 2003). The emulsifiers may be supplied to the manufacturer of the emulsion in a water-insoluble form and must be neutralised with an alkali or acid so as to produce the cationic or anionic water-soluble form, which, as mentioned by Salomon (2006), is used in preparing the soap solution. Moreover, to achieve specific properties, additives like anti-stripping agents, stabilisers, polymers, and coating improvers are also usually added (Thanaya, 2003; Salomon, 2006; Redelius and Walter, 2006).

As stated by Needham (1996), the bitumen droplet diameter in emulsions normally ranges from 1 to 30 μm, with the majority being <1 μm, while the largest mass or volume is between 5 and 10 μm, see Figure 2.6. However, the bitumen droplet size distribution is influenced by the recipe of the emulsion, by the bitumen emulsion's operational conditions and the mechanics (Salomon, 2006). For instance, when the emulsifier content is constant, the bitumen droplet size reduces as the stirring speed increases. When the stirring speed is constant, the droplet size of bitumen increases as the emulsifier content decreases (Jada et al., 2004).

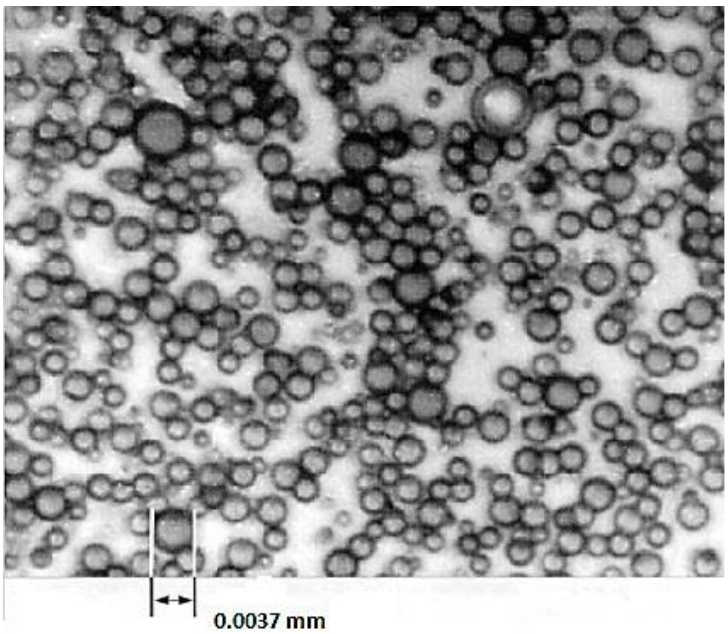

Figure 2.6 Bitumen droplets in an emulsion and their relative size (Chemarc, 2017).

2.4.3 Breaking Mechanism of Bitumen Emulsion

Bitumen emulsion has to revert to bitumen to act as binder, and this process is known as de-emulsification or breaking. The precise nature of bitumen emulsion breaking is yet to be understood completely, but it involves three crucial steps: flocculation, coalescence and water removal (Salomon, 2006; Redelius and Walter, 2006).

The interaction between two bitumen droplets is dominated by repulsive force when the bitumen emulsion is stable. Because of numerous factors, a decrease in the repulsive force causes the bitumen droplets to come into contact with each other through a process known as flocculation. In the flocculation process, water remains as a continuous phase, and as the flocs grow the bitumen droplets are bridged by creating cross-links between the flocs, in a process known as coalescence. In this process, bitumen is the continuous phase. In the last step, pure bitumen is formed after the water is removed by drainage, segregation, and evaporation.

Das (2008) stated that the breaking of emulsion relies heavily on the concentration as well as the type of the emulsifying agent. Therefore, the optimum balance between the breaking rate and stability is normally achieved by carefully selecting the emulsion pH, emulsifier concentration and type, and the size of the bitumen droplet (Ojum, 2015). Another factor is the charge on the emulsion. Anionic emulsions work more efficiently with aggregates that are positively charged, such as marble and limestone, whereas the cationic emulsions work better with aggregates that are principally negatively charged. As a result, making an appropriate emulsion-aggregate match offers a more rapid break, as well as improved adhesive properties. Figure 2.7 shows the possible stages while breaking a cationic emulsion.

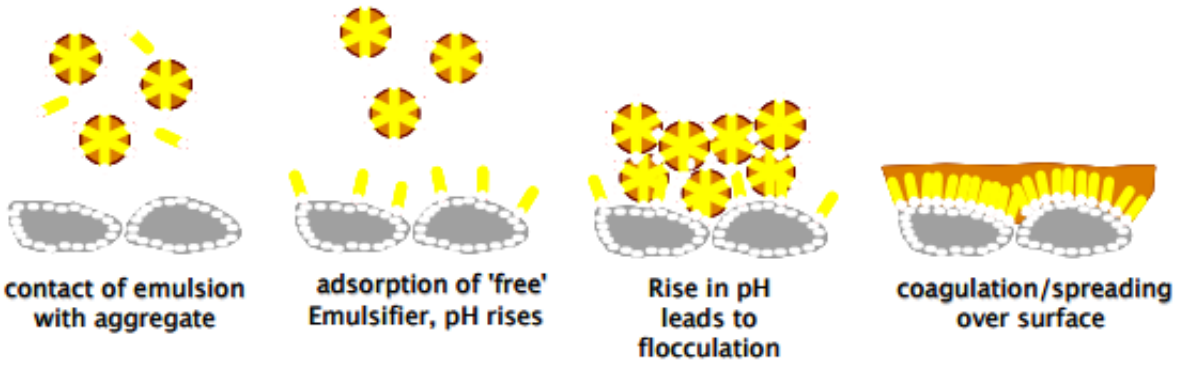

Figure 2.7 Stages in the breaking of a cationic emulsion (James, 2006).

2.4.4 Aggregate

CMA can be produced from different aggregate types as well as different gradations, including dense-graded or open aggregates, recycled asphalt pavement (RAP), or virgin aggregates.

In earlier times, semi-dense or open aggregate gradation was used in preparing the cold bituminous emulsion mixtures, in order to allow appropriate aeration in the high air-void mixture, facilitate evaporation of the trapped water and reduce the curing time (Nikolaides, 1983). Lately, even dense gradation is used because most of the water loss is achieved in the first weeks but some remains in the longer term (Oruc et al., 2006). Furthermore, gap-graded or continuous graded aggregates may be used (Ibrahim and Thom, 1997).

Cold in-place recycling has developed significantly, and its rationality has been demonstrated across the globe (Kim and Lee, 2006; Sebaaly et al., 2004; Bergeron, 2005). For instance, Ojum (2015) argued that, in Sweden, cold recycled bituminous emulsion mixtures may be used for base courses, wearing courses, or road bases.

2.5 Curing and Moisture Damage Protocols of CMA

Several researchers have applied different curing and moisture damage protocols in order to characterise the performance of CMA. The curing protocols of CMA have been identified, as the outcomes of some of the studies, and procedures for moisture damage protocols have also been proposed. The moisture damage protocols of CMA are usually applied after

a period of time. The following subsections provide a brief overview of the curing and moisture damage protocols.

2.5.1 Curing Protocol

According to Jenkins (2000), cold bituminous material curing is a process whereby water is discharged by the compacted and mixed material through evaporation. Water evaporation depends greatly on the weather conditions, which makes it hard for bitumen emulsions to cure properly when subjected to low temperatures, high humidity and rainfall immediately after application (AEMA, 2009). A number of studies have reported that full curing may take place after between 2 and 24 months in the field (Santucci, 1977; Leech, 1994; Thanaya, 2007). Different curing protocols proposed by researchers for South African conditions are summarised in Table 2.2.

Table 2.2 Amended curing procedures for cold mixes proposed between 1999 and 2004 (Jenkins and Moloto, 2008).

Curing Method	Equivalent Field Cure	Reference
24 hrs@ ambient+48 hrs@ 40^{0}C (OMC<8%) 45 hrs@ 60^{0}C (OMC>8%)	Emulsion mixes, medium term (1 year field cure)	Sabita (1999)
7 days@ ambient and 28 days@ ambient	Emulsion + cement Emulsion + no cement	Sabita (1999)
24hrs@ ambient in mould+3 days@ 40^{0}C(sealed)	6-month field cure (foam)	Asphalt Academy (2002)
24hrs@40^{0}C (sealed)+48hrs@40^{0}C ambient (unsealed)	Medium-term cure (foam and emulsion)	Robroch (2002)
24hrs@ ambient 25^{0}C (unsealed)+48hrs@ 40^{0}C (sealed)	Long-term foamed mix cure (1 to 2 years)	Houston and Long (2004)
24hrs@ ambient (unsealed)+48hrs@ 40^{0}C (sealed)	Medium-term cure (foam and emulsion)	Wirtgen (2004)
20hrs@ 30^{0}C (unsealed)+2x24hrs@ 40^{0}C (sealed-change bag midway)	Medium-term cure (foam and emulsion)	Stellenbosch University (2004)

As observed in Table 2.2, 40^{0}C was mainly used as the curing temperature so as to obtain the moisture conditions of the field after the curing process. Still, Serfass et al. (2004) observed that evaluation of the cured cold mixes in the laboratory is evidently required.

Oke (2011) believed that selecting suitable curing conditions in the laboratory, making sure there is sufficient shear strength in early life and choosing a suitable stiffness for the structural design life, are major problems. In their study, Serfass et al. (2004) noted that curing for 14 days at 35°C and 20% relative humidity is equivalent to almost 1-3 years in the field, under ambient temperature. On the other hand, Bocci et al. (2002) observed that curing for 14 days at 20°C is nearly comparable to 7 days at 40°C. Moreover, curing for 24 hours at 20°C, in addition to 24 hours at 40°C, corresponds to almost one to two weeks (Jenkins, 2000). The full curing protocol according to Thanaya (2003) is one day at room temperature plus one week at 40^0C plus another day at room temperature. Furthermore, Oke (2011) recommended that the curing protocol for early life is 40^0C for more than 12 hours, for intermediate life it is 40^0C for over 72 hours and for fully cured conditions it is 60^0C for more than 96 hours.

2.5.2 Moisture Damage Protocol

Semi-cured binder is vulnerable to damage from water during the curing period of an emulsion, because the bitumen is still in a semi-emulsified state (James et al., 1996). Therefore, water damage turns into a potential problem for normal cold mix. According to Oruc et al. (2007), determining water sensitivity of CMA requires the use of either the indirect tensile stiffness modulus ratio (SMR) or the indirect tensile strength ratio (ITSR). Several researchers have applied different curing protocols for CMA in water damage protocols in the laboratory (James et al., 1996; Brown and Needham, 2000; Oruc et al., 2007; Al-Busaltan et al., 2012; Al-Hdabi et al., 2013; Al-Hdabi et al., 2014). Al-Hdabi et al. (2014) and Al-Busaltan et al. (2012) used different curing protocols prior to obtaining the water damage protocol of 3 days at 40 °C, applying the water damage protocol prior to curing the specimens for 7 days, due to the fact that the specimens of the control mix showed very low strength at early age.

2.6 Performance Characteristics of CMA

Several studies have been carried out to evaluate the performance of CMA in terms of

mechanical properties. Through the outcomes of some of the numerous studies, the main problems of CMA have been identified, and methods for reducing them have been proposed. The performance of CMA is usually evaluated with reference to hot mix asphalt.

2.6.1 Effect of Compaction on the Mechanical Properties of CMA

Compaction is a significant factor that directly impacts CMA's mechanical strength. Therefore, several laboratory compaction methods such as static, Marshall, gyratory, and vibratory compaction have all been applied in previous studies. However, a debate has ensued on the compaction mechanism that occurs inside the mixture (Needham, 1996; Thanaya, 2003; Niazi and Jalili, 2009; Oke, 2011; Gómez-Meijide and Pérez, 2014a; Miljković and Radenberg, 2016). A case study by Khalid and Eta (1996) in which a Marshall hammer was used to compact the CMA, with 75 blows and 50 blows to each flat face is a good example. The porosity values found were 16.3% and 18.7%, respectively, which indicates that CMA requires heavy compaction to attain a reasonably les voids content. In another study by Serfass et al. (2004), it was evident that gyratory compaction significantly impacts the mechanical properties of CMA. From the findings, it was evident that the CMA stiffness modulus increases with increase in the degree of compaction, as shown in Figure 2.8.

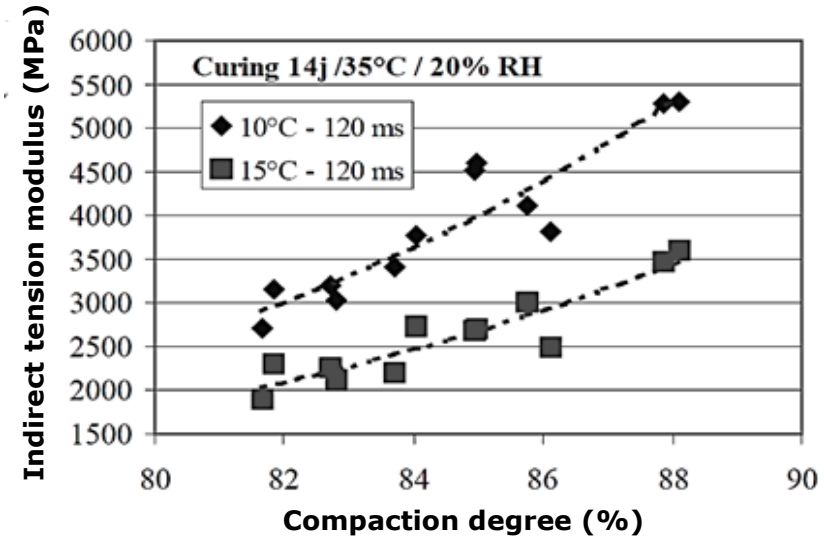

Figure 2.8 Effect of compaction degree on stiffness modulus of CMA (Serfass et al., 2004).

2.6.2 Effect of Curing on the Mechanical Properties of CMA through Addition of Ordinary Portland Cement

An early study by Terrell and Wang (1971) highlighted that Portland cement can overcome the low rate of curing the CMA. In this case, they utilised two types of anionic emulsion: slow setting and quick setting. They added 0-3% of Portland cement, according to the weight of the dry aggregate. As a result, Terrell and Wang (1971) cured the specimens under three conditions: (i) normal conditions, that is to say, 50% relative humidity, at a room temperature of 23.8^{0}C, for periods of one, three, seven and nine days; (ii) adverse conditions, at 90% relative humidity and a temperature of 4.4^{0}C; (iii) ultimate curing achieved after three days in the oven at a temperature of 48.9^{0}C. Terrell and Wang (1971) established that the development rate of the resilient modulus of emulsion-treated mixes was considerably fast-tracked by adding up to 3% cement for early curing. The resilient modulus increased by almost 200%, depending on the type of emulsion. In addition, they revealed that adverse curing conditions slowed down the curing action, when compared to other curing conditions. Nevertheless, adding 1% cement into the mixture solved the delay experienced during the curing process. The effect of adding cement to improve the strength of emulsion-treated mixes that were developing slowly, was investigated by Schmidt et al. (1973), where 1.3% and 3% of cement was added to the mixture. They established that with cement the emulsion-treated mixes cured faster, were more resistant to damage caused by water, and had a higher resilient modulus which developed more rapidly. Head (1974) investigated the effect of cement, curing time and temperature on CMA performance, which was based on the modified Marshal Stability Test using 0-2% cement. He cured the specimens at temperatures of 4.4^{0}C and 10^{0}C for periods of one, three, five, and seven days. Moreover, he cured three cement-treated specimens at a temperature of 49^{0}C for 3 days so as to achieve full curing. He observed that adding cement had a significant impact on the Marshall stability; specifically, the addition of 1% cement led to a 250-300% increase in stability, compared to the samples that had no cement while curing at a temperature of 4.4^{0}C. Furthermore, he established that, when

cured at a temperature of 10^0C, the stability increased from 272kg on day one to 363kg on day seven. Without additives as mentioned by Needham (1996), CMA cannot achieve the level of stiffness that the hot mix can. Head's (1974) test results showed an increase both in the rate of curing and in the ultimate stiffness modulus, as evidenced in Figure 2.9.

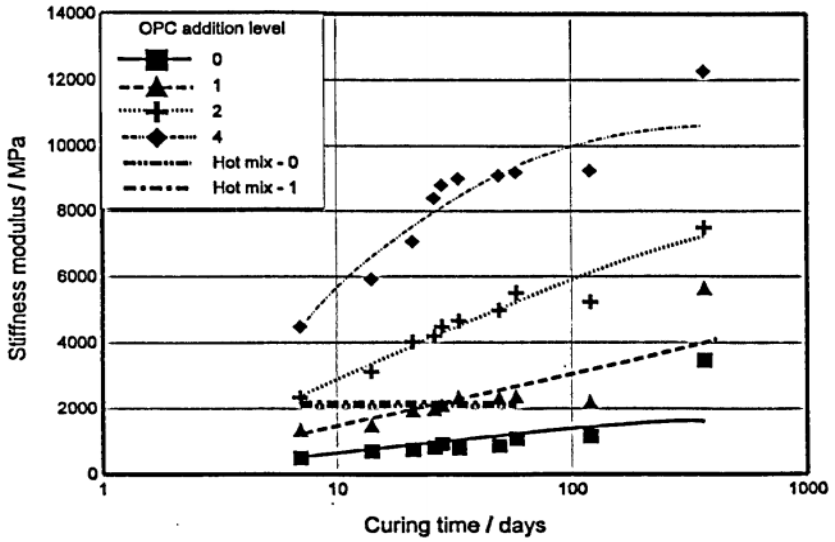

Figure 2.9 Effect of Ordinary Portland cement (OPC) on stiffness modulus over curing time (Needham, 1996).

Li et al. (1998) also evaluated the mechanical properties of CMA with Portland cement. This study showed the performance of CMA with Portland cement gaining beneficial properties such as longer fatigue life and higher toughness. Moreover, Oruc et al. (2007) evaluated the mechanical properties of CMA with 0-6% of Portland cement. The results also indicated a considerable enhancement with high Portland cement additions. Figure 2.10 shows the permanent deformation resistance of CMA specimens using different cement contents cured at 40^0C in the repeated load axial test (RLAT). Furthermore, García et al. (2013) studied the effect of cement content at 20^0C using different relative humidities on CMA. The results of the study revealed that CMA without Portland cement is less rigid and resists much lower forces than hot mix asphalt, even for 28 days of curing at a significantly low relative humidity. However, in the case where part of the filler (1.5–6 % by mass) is replaced by Portland cement, the Marshall strength and rigidity increase

progressively. Figure 2.11 shows the Marshall strength of CMA with different amounts of Portland cement at different curing times with 90 % ambient relative humidity.

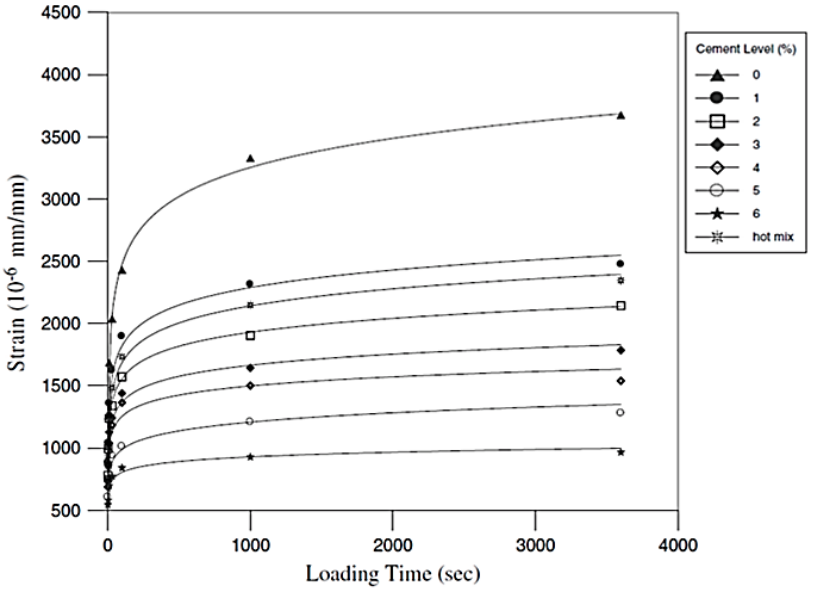

Figure 2.10 Effect of different cement content on CMA permanent deformation resistance (Oruc et al., 2007).

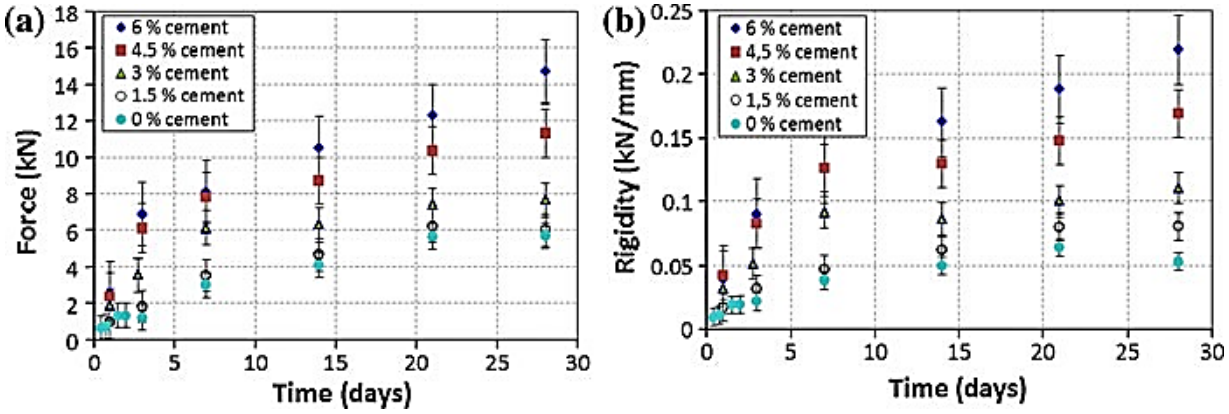

Figure 2.11 a) Marshall strength (kN) with time and b) Rigidity (kN/mm) with time, for CMA with different amounts of Ordinary Portland cement (OPC) cured at 90 % environmental humidity (García et al., 2013).

2.6.3 Effect of Curing on the Mechanical Properties of CMA through Addition of Rapid Hardening Cements

Limited studies have examined the use of rapid-hardening cements to improve the

performance of CMA (Thanaya, 2003; Fang et al., 2016). For example, Thanaya (2003) recommended adding 1-2% rapid-hardening cement instead of using Portland cement to increase early life strength of CMA. The findings of the study revealed that CMA can gain stiffness modulus values of 2000-2500 MPa in only 2 weeks through adding 2%, rather than 16 weeks for CMA without rapid-hardening cement. However, Fang et al. (2016) found that the Marshall stability at 28 days for the CMA with 6 % of calcium sulfoaluminate cements (CSA) and calcium aluminate cements (CAC) was less than for the HMA in the case of cationic emulsion, while for the anionic emulsion it was much closer to the HMA's stability in the case of CSA cement, or even higher in the case of CAC. Moreover, Fang et al. (2016) argued that the increase in the early strength of CMA was attained not only due to the rapid hardening and setting properties of this kind of cement, but also due to the fact that they bind a higher amount of water than Portland cement, as shown in Figure 2.12.

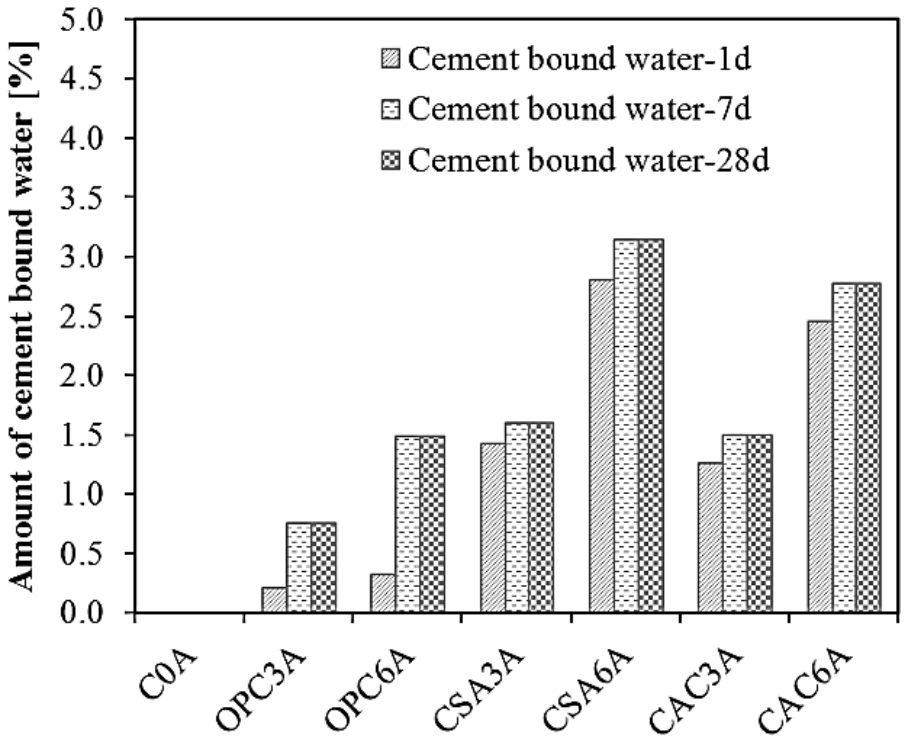

Figure 2.12 Amount of water bound for the CMA specimens with 0%, 3% and 6% of Ordinary Portland cement (OPC), calcium aluminate cements (CAC) and calcium sulfoaluminate cements (CSA), after 1, 7 and 28 days curing (Fang et al., 2016).

2.6.4 Microstructure of CMA

The microstructure of CMA has been investigated in previous studies. For example, García et al. (2013) demonstrated the detail of the CMA's inner microstructure treated with cement, using an X-ray technique. García et al. (2013) argued that the bubbles, as shown in Figure 2.13(a), possibly appeared because of a suboptimal compaction of the mixture. Air entrainment emanating from the emulsifier in the emulsion is the other probable cause of the bubbles, a point that was confirmed by Pouliot et al. (2003). The other feature evident in the microstructure indicated in Figure 2.13(a) is some degree of aggregate de-bonding that may be overcome using a different method of compaction and adhesion promoters (García et al., 2013). Another example by Fang et al. (2016) displays a cross-section of CMA with an approximate diameter of 5 mm (see Figure 2.13(b)). The aggregates revealed some cracks that may be caused by sample preparation. Figure 2.13(b) also reveals a large amount of air voids. Pouliot et al. (2003) observed that the CMA air-void content could be as high as 10% at the end of the 28 days thereby exceeding that in HMA (4%). However, this depends on the amount of bitumen (Yan, 2012). From this observation, one could argue that CMA is likely to suffer more from water damage than dense HMA, resulting in de-bonding because of the large amount of air voids (Fang et al., 2016).

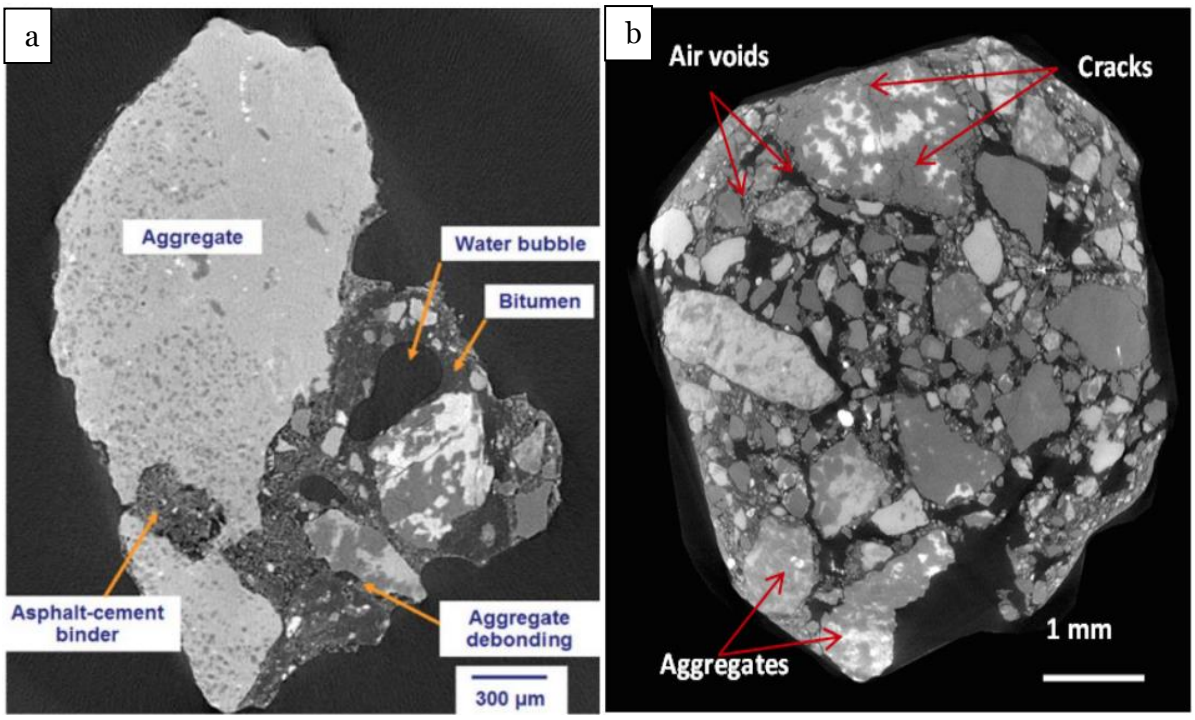

Figure 2.13 (a) Micro CT image of a cement and asphalt composite (García et al., 2013) and (b) Micro tomography detail of CMA (Fang et al., 2016).

2.6.5 Effect of Water Damage on the Mechanical Properties of CMA

The impact of cement on the resistance of CMA to water damage has been observed by a number of authors (James et al., 1996; Nassar et al., 2016; Oruc et al., 2007; Brown and Needham, 2000; Al-Hdabi et al., 2014). In the study conducted by James et al. (1996), the CMA specimens were cured at a temperature of 20^0C with, and without, cement for 10 days and then they were soaked under vacuum and stored in water for twenty days. The study revealed bad cracks in the CMA specimens without cement. The CMA specimens did not show any measurable stiffness modulus. On the other hand, the stiffness modulus for CMA specimens with cement was found to be approximately 1200 MPa, which exceeds half the value obtained for un-soaked specimens. In another study, Brown and Needham (2000) observed the water damage in CMA specimens with, and without, any additives of calcium chloride ($CaCl_2$), hydrated lime (H.lime) and Portland cement (under two dissimilar soaking protocols) that had been cured at 20^0C for 11 days. They found that the CMA specimens containing Portland cement had greater stiffness as compared to the other

mixtures, after 5 and 12 days in water at room temperature. Moreover, Oruc et al. (2007) considered CMA and HMA specimens with 0%, 1%, 2%, 3%, 4%, 5% and 6% of cement, which were cured at a temperature of 25^0C for 3 days. Then, the CMA and HMA specimens having, and lacking, cement were soaked for 1 day in water at 50°C. They established that CMA specimens lacking cement failed after the sixth hour of conditioning, whereas the resistance to water damage of CMA specimens was raised by the addition of cement, as shown in Figure 2.14. In addition, the findings indicated that cement is an effective adhesion agent for CMA.

However, Al-Hdabi et al. (2014) used specimens with, and without, cement at different curing protocols prior to applying the water damage protocol (3 days at 40 °C). The water damage protocol was found to be critical; when water was applied before curing for 7 days, specimens of the control mix revealed very low strength at early age. These curing protocols of 7 days were studied by Nassar et al. (2016) in their quest to assess the water damage of CMA specimens with fine ash (FA), granulated blast furnace slag (GGBS), ordinary Portland cement (OPC), and limestone filler (LF). The results of the study showed that the indirect tensile strength ratio (ITSR) for the CMA specimens with OPC exceeded that of the other mixtures, as indicated in Figure 2.15 below. In addition, Nassar et al. (2016) indicated that the higher ITSR values may have a relationship with additional activation of cement hydration.

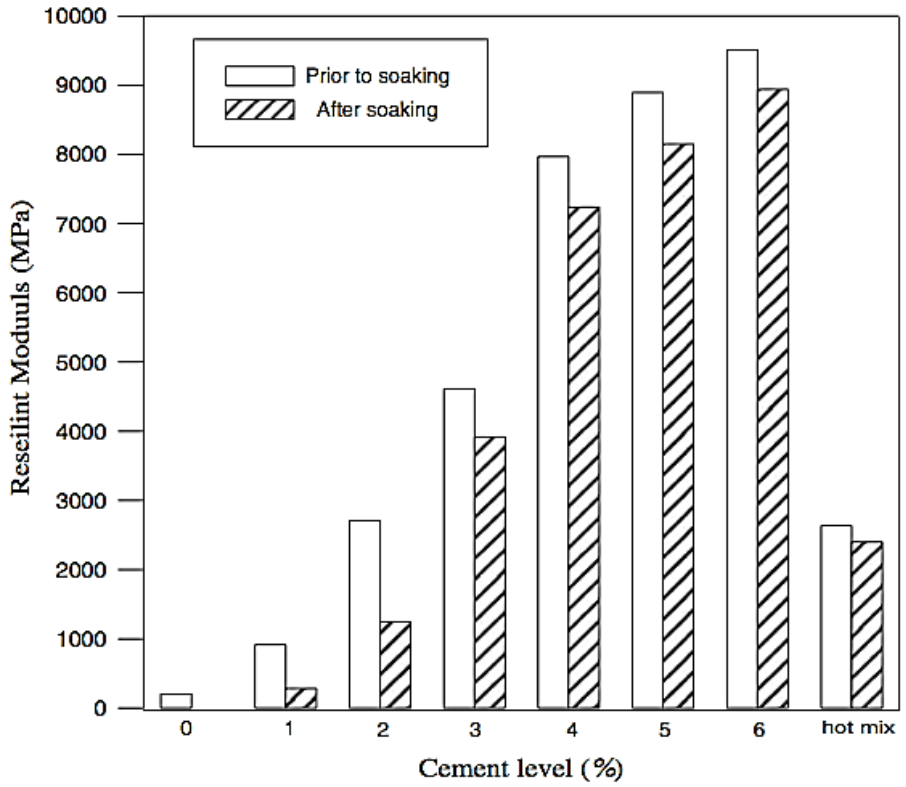

Figure 2.14 Influence of CMA with different amounts of cement on resistance to water damage (Oruc et al., 2007).

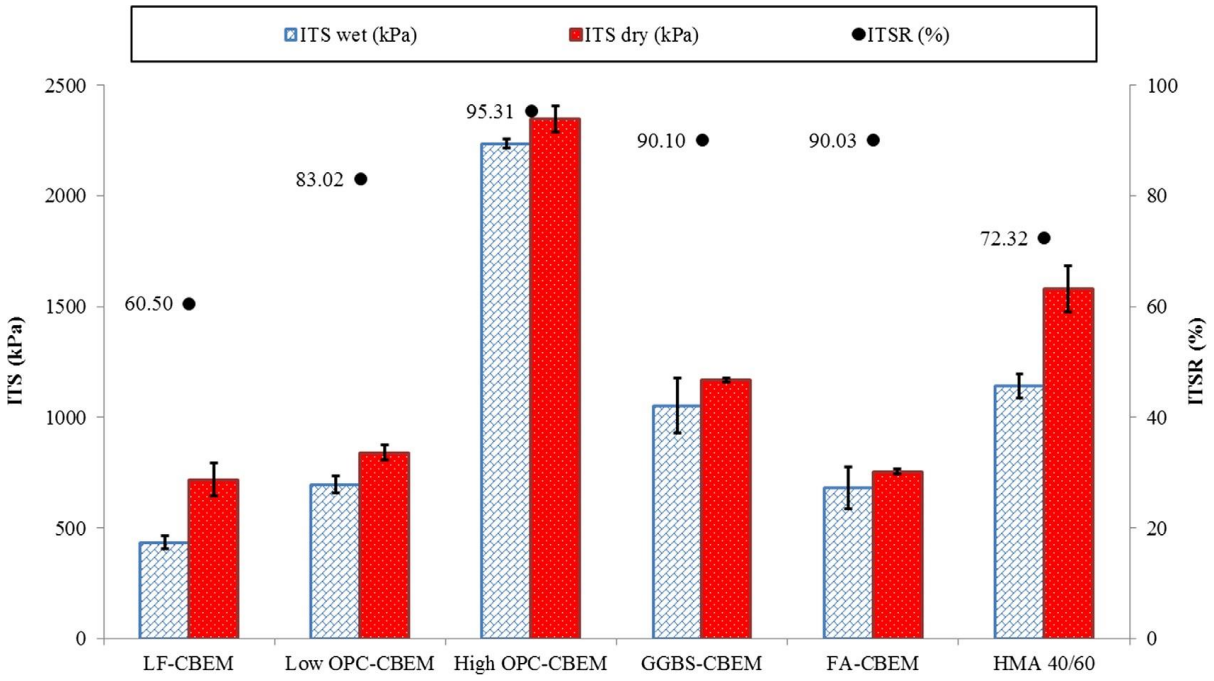

Figure 2.15 Moisture damage at different additives content on CMA (Nassar et al., 2016).

2.7 Encapsulation Techniques

2.7.1 Introduction

Generally, the technique of encapsulation is a process wherein droplets or small particles are coated to add useful properties. Capsules have been described by Silva et al. (2014) as particles that have an inner core of an active substance that is covered with a polymer layer. For this reason, the particles may be classified into the following types: Polynuclear, Mononuclear and Matrix, (as shown in Figure 2.16).

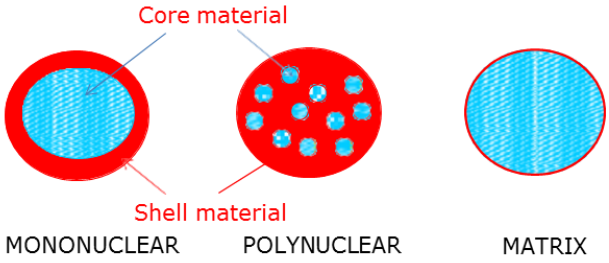

Figure 2.16 Types of microcapsules (Bevilacqua et al., 2010).

According to Favaro-Trindade et al. (2008), Polynuclear and Mononuclear capsules are differentiated by how the core is divided (as shown in Figure 2.17). Matrix system cores as mentioned by Silva et al. (2003), are uniformly dissolved and/or dispersed in a polymer network, see Figure 2.18.

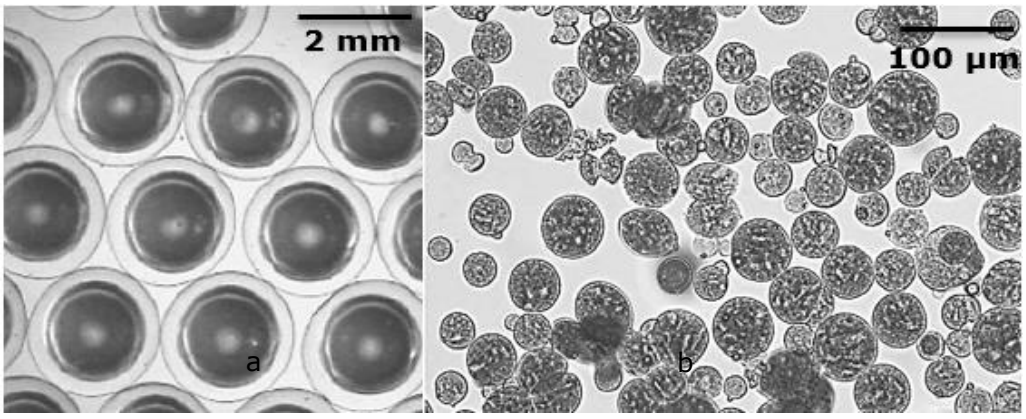

Figure 2.17 (a) Mononuclear capsules containing solvent (Stark et al., 2003) and (b) Polynuclear microcapsules containing milk protein (Heidebach et al., 2009).

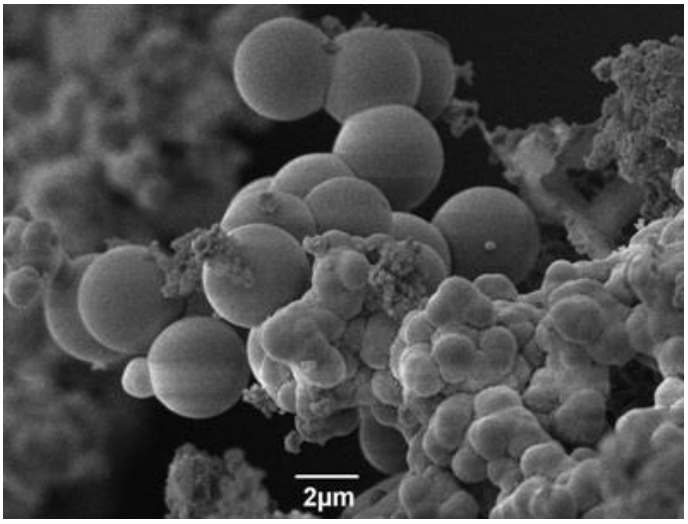

Figure 2.18 Matrix microcapsules containing silica (AZoMaterials, 2013).

Mallepally (2009) asserts that Carbonless copy paper was the first commercial product in history to use microcapsules. The microencapsulated colourless ink coating is applied on top of the paper sheet and the developer is then applied to the next sheet. When writing, pressure is applied, leading to the breaking of the capsules. As a result, the developer and the ink react to generate a dark coloured copy. Carbonless copy paper is still the most important product that uses microencapsulation technology, and is still produced commercially (Dubey, 2009). Microencapsulation technology has been used in many areas including the agricultural, pharmaceutical, food and medical industries through the encapsulation of such things as microorganisms, colourings, essential oils, sweeteners and flavourings. Ghosh (2006) states that the pharmaceutical industry used microencapsulation technology for many years to prepare capsules containing active ingredients. Also, the textile industry used microencapsulated materials to improve the properties of finished goods (Jyothi et al., 2012). The most notable application is the incorporation of microencapsulated Phase Change Materials (PCMs). The PCMs absorb and release heat according to the changes in the environmental temperatures. That is to say, an increase in temperature results in the melting of the PCMs since they absorb heat, while a decrease in temperature leads to solidification of the PCMs as they release heat. The food industry has increasingly exhibited some complex formulations, such as microorganisms in fermented meat and adding polyunsaturated fatty acids in ice creams,

yogurts and milk, which are vulnerable to auto-oxidation. Also, in instant foods the use of flavour compounds which are extremely volatile, can only be obtained through microencapsulation (Khan et al., 2011; Gharsallaoui et al., 2012). In addition, healing is achieved by including a triggering chemical catalyst and microencapsulated agent on a matrix of epoxy for healing (White et al., 2001). A developing crack breaks trapped microcapsules, giving out a healing agent into the plane of a crack via capillary action. Healing agent polymerization is started by entrapped catalyst contact, sealing the face of the crack. The place-specific autonomic control of repair is provided by the damage initiated triggering process.

This encapsulation technique has been used in various methods in different fields. Some of these are listed in Table 2.3 below:

Table 2.3 Overview of common microencapsulation processes.

Technology	**Application**	**Particle size (μm)**	**Ref.**
Spray Drying	Food industry, Pharmaceutical Industry	10-400	(Gharsallaoui et al., 2007; Gouin, 2004; Jain et al., 2012)
Freeze Drying	Food industry, Pharmaceutical Industry	20–5,000	(Madene et al., 2006)
Spray Cooling	Food industry, Pharmaceutical Industry, Chemical Industries etc.	20-200	(Dewettinck and Huyghebaert, 1999; Mishra, 2015)
Extrusion	Food industry, Industrial Ceramics, and Electronic Components.	300–5,000	(Nedovic et al., 2011; Mishra, 2015)
Coacervation	Textile Industry, Drug Delivery	10-800	(Jyothi et al., 2010; Zuidam and Nedoviæ, 2010; Arshady, 1990; Nimmannit and Suwanpatra, 1996)
Pickering emulsion	Food, Cosmetics, Pharmaceutics, Oil Recovery etc.	0.75-100	(Katepalli, 2014; Mishra, 2015)

In the following paragraphs, different types of fabrication techniques are detailed.

2.7.2 Spray Drying

Spray drying is an encapsulation technique that involves forming an emulsion, suspension or solution that has a core and wall material (Silva, 2014). Once the emulsion has been formed, it is subjected to nebulization, where the emulsion or suspension is dried in a chamber by subjecting it to hot air (Figure 2.19). The heating process results in the evaporation of all the water content, resulting in the material encapsulating (Laohasongkram, 2011). Spray drying as a microencapsulation method has been widely used in many industries, such as in the food industry to encapsulate food flavours and lipids and for pigmentation, among other uses (Gharsallaoui et al., 2007). The microcapsules fall within the range of 0.2-5000 μm and take different shapes depending on the material and technique used in preparation. However, the application of this spray drying encapsulation method is limited to certain areas such as essential oils and microorganisms because the temperatures required can result in destruction of the products.

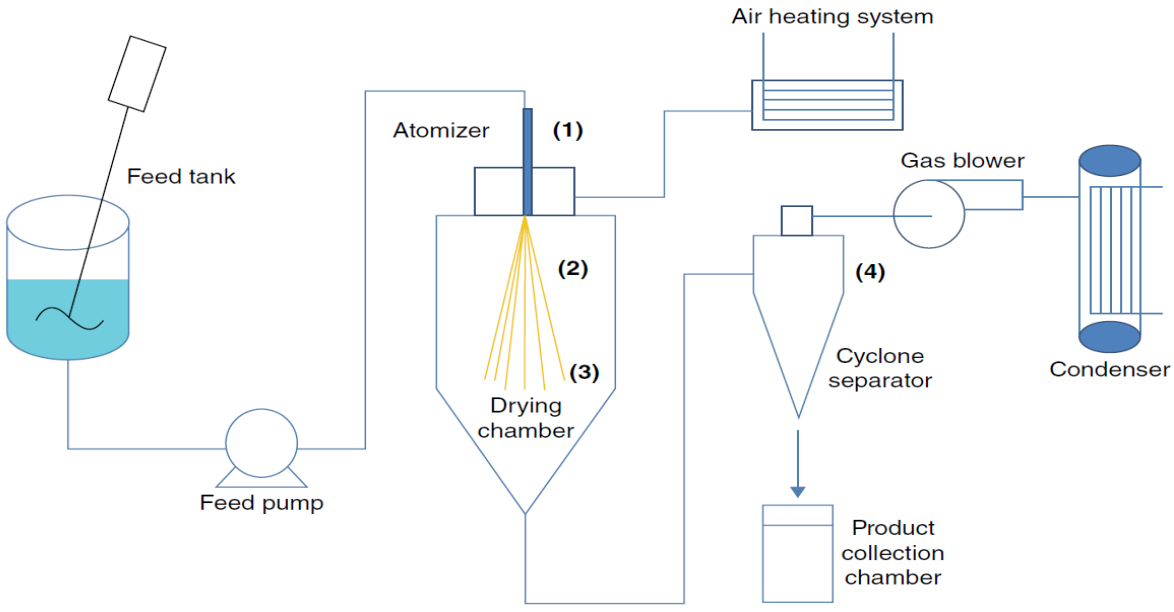

Figure 2.19 Spay drying process: (1) Atomization (2) Spray – hot air contact (3) Evaporation of moisture (4) Product separation (Anandharamakrishnan, 2015).

2.7.3 Spray Cooling

Spray cooling is the other commonly used encapsulation technique. Unlike spray drying, where emulsions are dried by subjecting the contents to hot air, spray cooling does not involve evaporation of solvents (Kirk, 2008). Instead, in spray cooling, the solvents are subjected to lower temperatures below the melting point, to allow the solution to solidify. The particles used in spray cooling range from 20 μm up to 200 μm. Nevertheless, very small particles are likely to cause problems that include low encapsulation capacity, as well as the destruction of the core during storage. Spray cooling is widely used for encapsulating vitamins and minerals (Rathore et al., 2013). Figure 2.20 is a schematic diagram of the preparation of the spray cooling method.

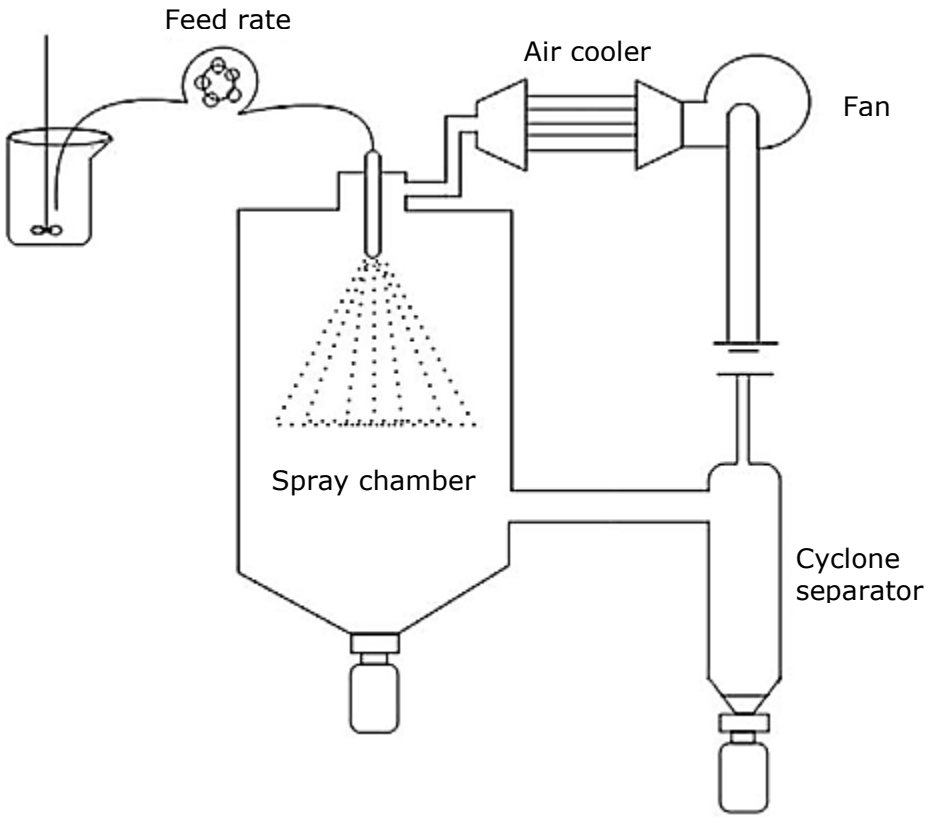

Figure 2.20 Scheme of spray cooling equipment (Okuro et al., 2013).

2.7.4 Coacervation

Coacervation is a common encapsulation method that involves forming a liquid rich

polymer phase using another liquid phase (Zuidam and Nedoviæ, 2010), see Figure 2.21. Depending on the types of polymers present, the coacervation process can be classified as simple or complex. In simple coacervates, only a single polymer is used, whereas in complex coacervates, two or more polymer types with different properties are used. Coacervation is a desirable encapsulation technique because of its simplicity and the fact that it is a low-cost process. The sizes of particles depend on a number of factors that include stirrer shape, stirring velocity, viscosity, and surface tension, with the particle sizes ranging from 10μm to 800μm. The major shortcomings associated with coacervation are the fact that the process only occurs under limited pH ranges, colloid density, and/or electrolyte concentrations (Comunian et al., 2013).

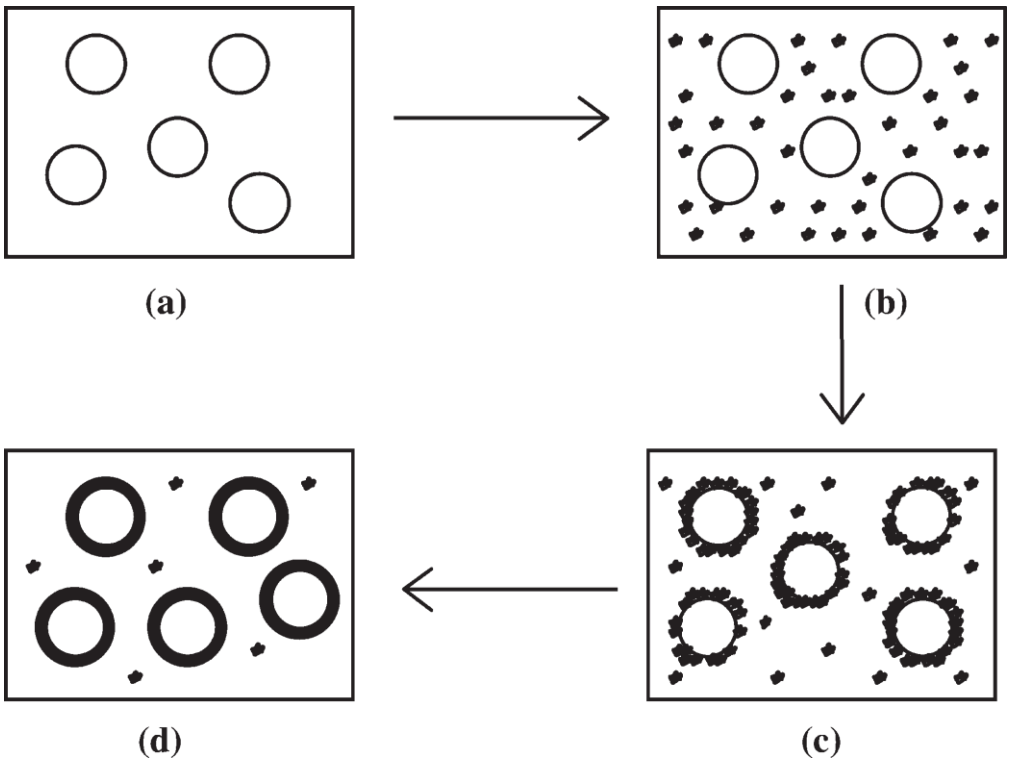

Figure 2.21 Schematic representation of the coacervation process: (a) Core material dispersion in shell polymer solution; (b) Coacervate separation from solution; (c) Coating of core material (d) Coalescence of coacervate to form continuous shell (Redrawn from Jyothi et al., 2010).

2.7.5 Lyophilisation

Lyophilisation, otherwise called freeze drying, is an encapsulation technique that involves

the removal of moisture content from the frozen materials under the vacuum sublimation method (Chen and Wang, 2007). This implies that the moisture content is drained out without necessarily subjecting the specimen to high temperatures. The particle sizes of lyophilisation fall within the range of 20-5000μm. Lyophilisation has many advantages. For example, it creates good quality products since the sample is not subjected to high temperature. Because of this, the technique is widely used in flavourings. However, the major shortcoming associated with this method is that it is a lengthy and costly process. To some extent this undermines its usefulness (Marques et al., 2006). Figure 2.22 is a schematic diagram of the preparation of the spray freeze drying method.

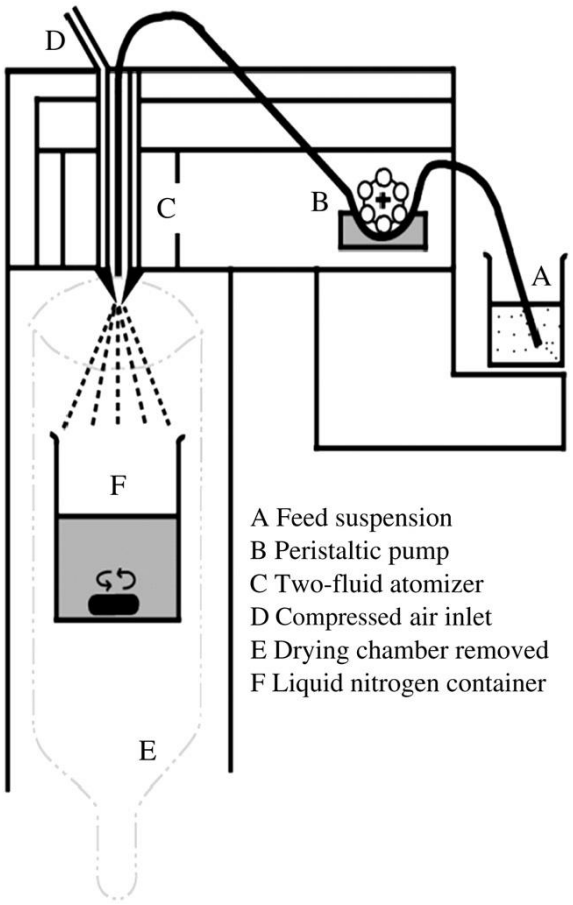

Figure 2.22 Schematic diagram of spray freeze drying method (Kho and Hadinoto, 2011).

2.7.6 Pickering Emulsion

Pickering emulsions are any kind of emulsion, be it water-in-oil, oil-in-water or a mixture of both, maintained by solid particles enabled by surfactants (Aveyard et al., 2003; Binks, 2002; Binks and Horozov, 2006). Figure 2.23 shows an image from scanning electron microscopy (SEM) of a colloidosome comprising a droplet of oil in an aqueous state, covered by polystyrene particles measuring 0.9μm in diameter. Additionally, the method can be scaled up with ease. However, the major disadvantage of the Pickering emulsion method is the costly process of removal of things like vegetable oils. Furthemore, the technique requires a vigorous cleaning of microspheres for vegetable oil residue removal (Zuidam and Nedoviæ, 2010).

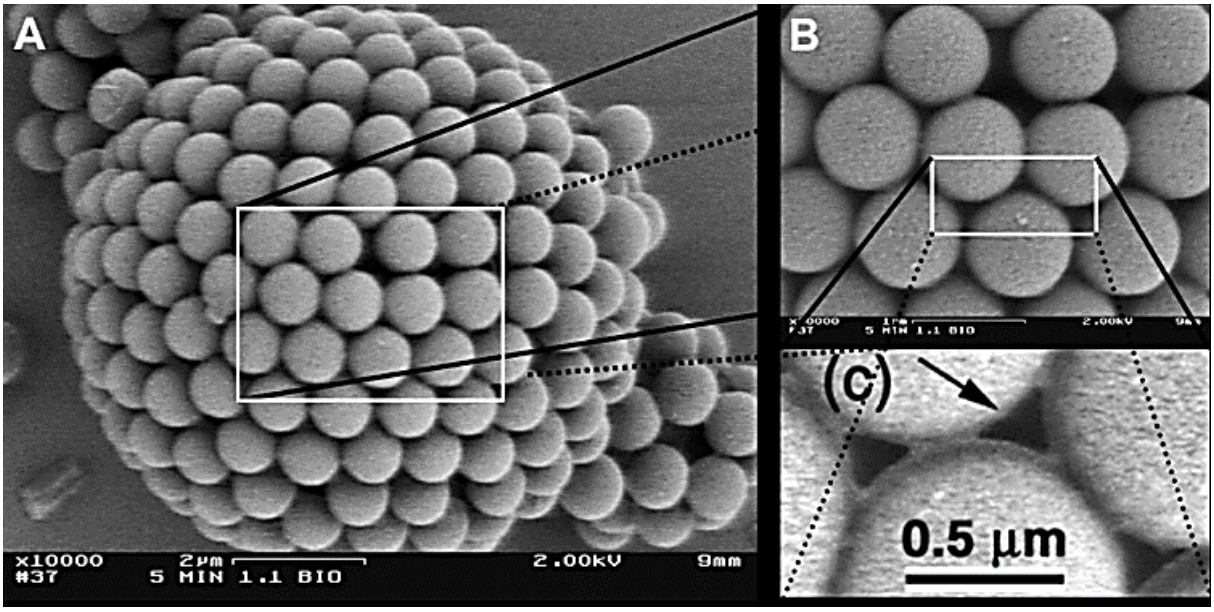

Figure 2.23 Scanning Electron Microscopy (SEM) images of a typical colloidosome showing (a) the assembly of colloidal particles on the interface of an emulsion droplet and (b) and (c) the pores (open space between particles) that control permeability (Dinsmore et al., 2002).

2.7.7 Extrusion

Extrusion is an encapsulation technique that involves turning hydrocolloids into microcapsules (King, 1995). The hydrocolloid gelations such as pectin, carrageenan and

alginate, contained in mineral contents, have been widely used in entrapping bacteria using the extrusion method. For, the production of bacteria capsules with hydrocolloids such as alginate, alginate solution is prepared and then microorganisms are added into it. Then, using an extruder (pilot scale) or a needle (laboratory scale), the suspension is extruded as droplets into the calcium chloride solution, as shown in Figure 2.24.

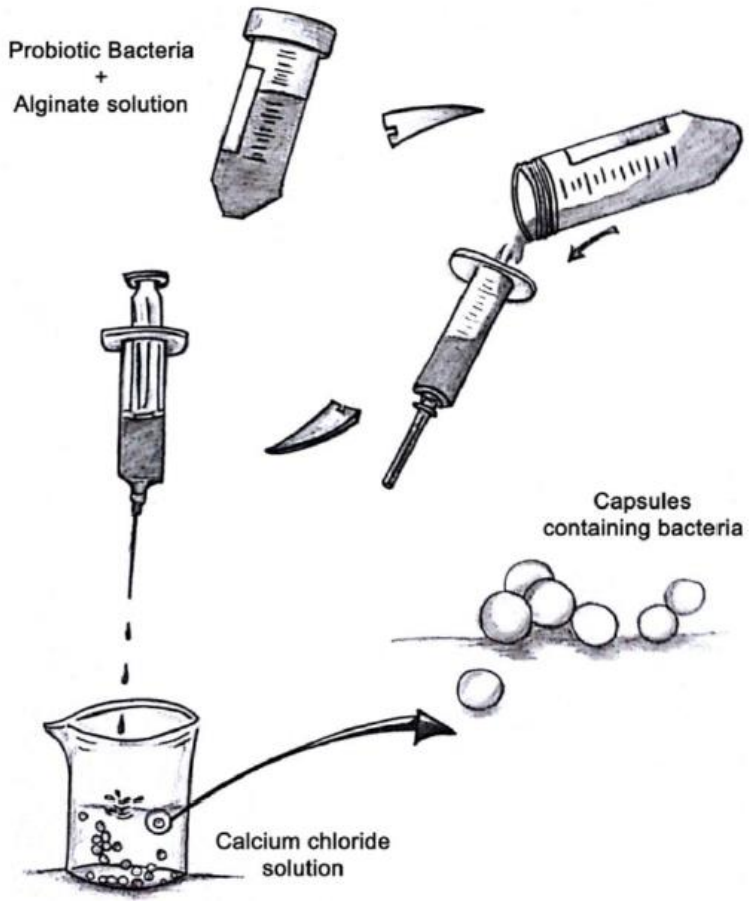

Figure 2.24 Schematic diagram of the extrusion encapsulation method (Serna-Cock and Vallejo-Castillo, 2013).

2.8 Assessing Physical Characteristics of Capsules

The dissolution properties and performance with active ingredients of encapsulates are frequently associated with their physical properties. Density is a physical characteristic which depends on the experimental technique used and on the structural properties of capsules (Kelkar et al., 2011). Electron and optical microscopy have been used extensively

to offer essential information regarding shell thickness, surface topography, size distribution, and shape in food products. These properties can be measured by techniques such as Scanning Electron Microscopy (SEM), environmental scanning electron microscopy (ESEM), Confocal Laser Scanning Microscopy (CLSM) and optical microscopy.

2.8.1 Scanning Electron Microscopy (SEM)

Electron Microscopy (EM) utilises an electron beam to form a specimen image (Bozzola and Russell, 1992; Heath, 2005). SEM is among the most widely used instruments in laboratories for the research of the microstructure of materials and it is common in different forms in fabrication plants (Chandlerm and Seraphin, 2002). SEM provides information about topographical features, phase distribution, morphology, compositional differences, crystal orientation, crystal structure, and the location and presence of electrical defects. Beneficially, SEM is able to evaluate samples of varying scale from nanometer to centimetre (Rouche et al., 2006; Shu et al., 2006; Weiβ et al., 1995; Yan-yu et al., 2006). For example, the double shell layers from microcapsules can be found in SEM tests (shown in Figure 2.25). However, environmental scanning electron microscopy (ESEM) provides more advanced abilities compared to SEM (Zuidam and Nedoviæ, 2010). The SEM requires a high vacuum in the specimen chamber to avoid atmospheric interference with primary or secondary electrons, while the ESEM can be operated with a low vacuum (up to 10 Torr of vapour pressure) in the specimen chamber, which allows the investigation of the surface tomography of wet encapsulates (Ren et al. 2007).

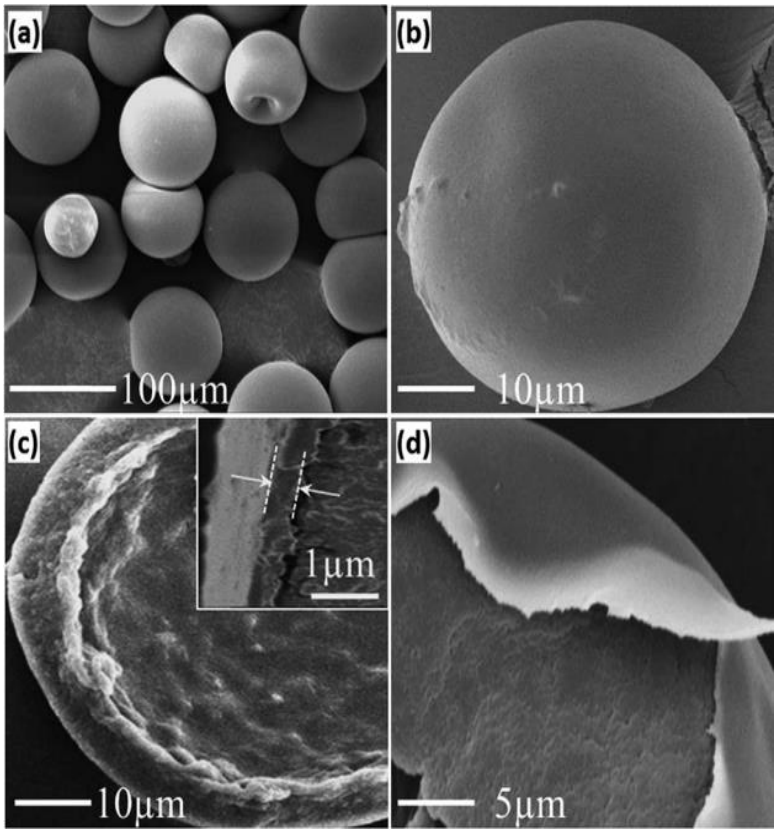

Figure 2.25 SEM images of double-layered polyurea microcapsules containing hexamethylene diisocyanate (HDI) (Sun et al., 2012).

2.8.2 Optical Microscope

An upright typical optical microscope has the ability to characterise structures which measure 0.2μm or more as restricted by the light wavelength (Zuidam and Nedoviæ, 2010). Frequently, specimen video images or digital images are taken, and then they are analysed quantitatively by using an image evaluation software. For example, citronella oil was observed under an optical microscope by Hsieh et al. (2006), embedded in chitosan microcapsules by using orifice dispensation. The outcomes demonstrated that good microcapsule dispersion and formation were found by using a mixture of 0.5wt% natural coconut oil, 0.5wt% NaOH, and 0.5wt% chitosan as shown in Figure 2.26.

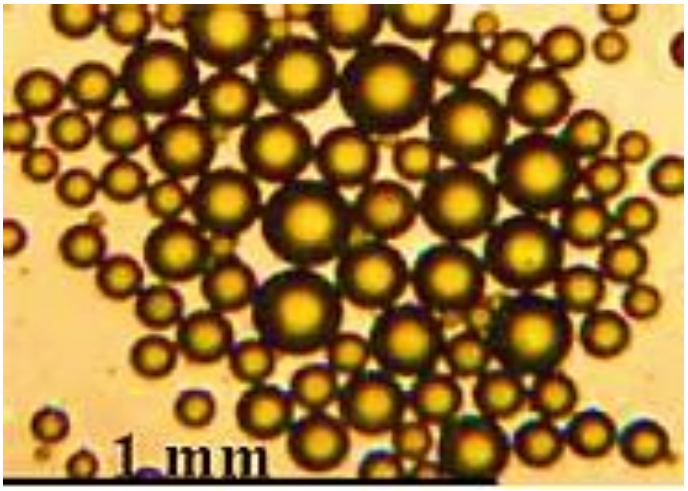

Figure 2.26 Chitosan Microcapsules Microphotograph. The microcapsules were made at 0.5wt% natural coconut oil, 0.5wt% NaOH, and 0.5wt% Chitosan at a stirring rate of 800 rpm (Hsieh et al., 2006).

2.8.3 Confocal Laser Scanning Microscopy (CLSM)

According to Zuidam and Nedoviæ (2010), optional sectioning of Confocal Laser Scanning Microscopy (CLSM) can produce in-focus images of a fluorescent specimen. A point laser source illuminates the fluorescent specimen, and each volume element of the specimen is related to the discrete fluorescence intensity. It is possible to obtain images of a thick object point-by-point, though a computer software package can reconstruct its three-dimensional structure. The use of gum arabic and gelatin to encapsulate an oil-based active ingredient through a complex coacervation process is a good example. Fluorescent markers are used to label the polymers. CLSM identifies the spatial distribution of both gum Arabic and gelatin throughout the encapsulate shell (Lamprecht et al. 2000). The addition of fluorescently labelled casein to the coacervation process as a macromolecular model compound produces a graded distribution of casein in the shell materials as shown in Figure 2.27. It was observed that casein had the greatest concentration at the oil-wall interface. Another study demonstrated CLSM to be effective in observing cross-linking ions in alginate-poly-l-lysine (PLL)-alginate encapsulates made by fluorescently-labelled polymers and evaluating the distribution of polymers (Strand et al. 2003).

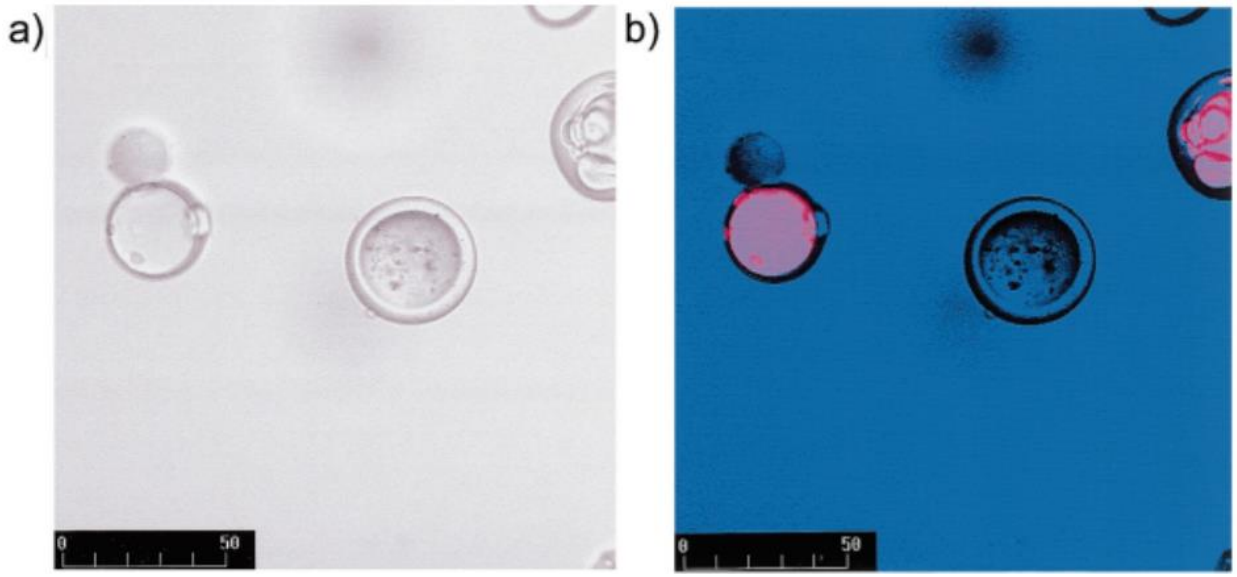

Figure 2.27 Microcapsules containing a nile red stained oil phase, (a) a light microscopy image and (b) CLSM using the red fluorescence channel and transmitted light detection (Lamprecht et al. 2000).

2.8.4 X-Ray Micro-Computed Tomography (X-Ray Micro-CT)

X-Ray Micro-CT is a technique used to produce three-dimensional complex structures containing a spatial resolution in the range of a micrometre (Zuidam and Nedoviæ, 2010). X-Ray Micro-CT can be employed for 3D image reconstruction with high internal object structure resolution. For example, Mayo et al. (2012) used X-Ray Micro-CT to examine the self-healing properties of Polystyrene. This involved Poly (Methyl methacrylate) composite polymer material, which was made up of Dichlorobenzene (DCB) solvent and capsules with a diameter of about 60μm. The CT-scan analysis clearly showed the absence of full capsules in the plane of the crack. In addition, there was a larger number of empty capsules in the aged sample, as shown in Figure 2.28.

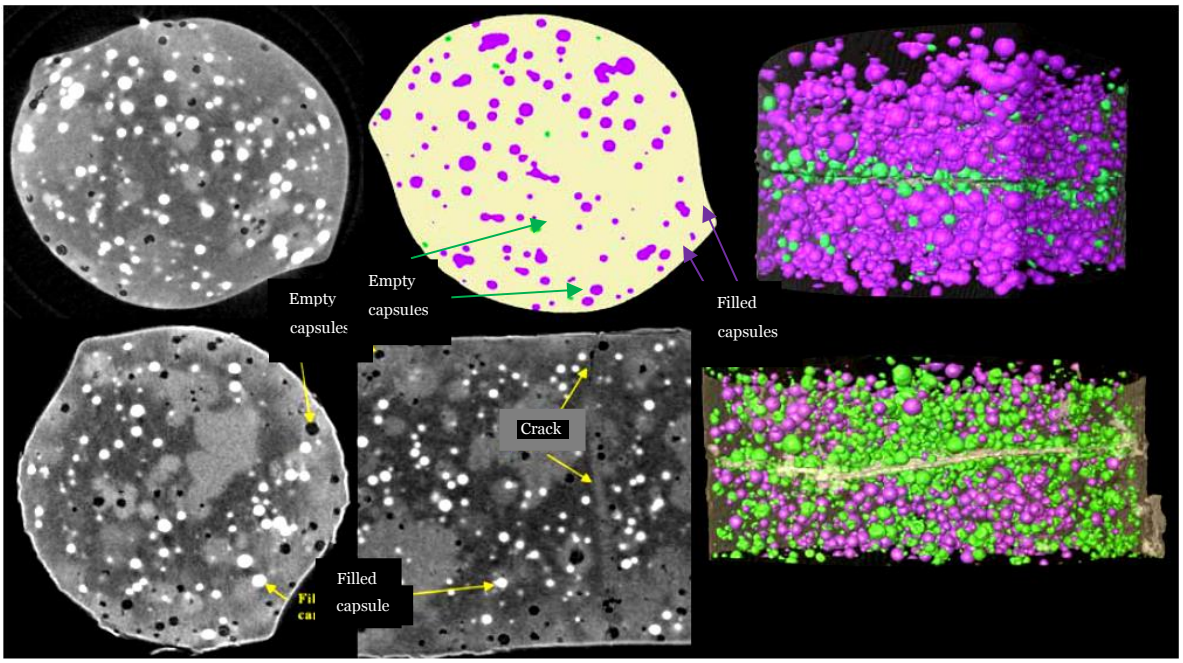

Figure 2.28 CT scan image of self-healing polymer through material (capsules) (Mayo et al., 2012).

2.9 Assessing Chemical Composition of Capsules

Several researchers have used different techniques to determine the chemical composition of capsules. For example, a study by Lamprecht et al. (2000) of the chemical composition of an encapsulated sample was determined from gravimetric analysis, based on the initial concentration and the amount extracted from the capsules and from the volume and density of the dry capsules, by using a Gas Pycnometer. In another example by Peniche et al., (2004), the moisture content of an encapsulated sample is determined from the weight loss during heating in a microwave oven. The inorganic matter of the sample is determined gravimetrically by heating at 550°C in an open vessel under air with constant weight. Moreover, in a study by García et al. (2011) different techniques were used to analyse the chemical composition of capsules that consist of cement, liquid epoxy resin, porous sand and four different types of rejuvenators. Each encapsulation material had a density of 2.315 g/cm^3 for the porous sand, 3.141 g/cm^3 for the cement, 1.127 g/cm^3 for the epoxy and 0.962 g/cm^3, 0.922 g/cm^3, 0.983 g/cm^3, and 0.920 g/cm^3 for the four rejuvenators. A CT-scan was used to determine the volumetric relationship between the

shell and the core of the capsules. Thermo-gravimetric analysis (TGA) was used to investigate the remaining mass of the capsules at 1000°C in N_2 atmosphere. Furthermore, in a study by Al-Mansoori et al. (2016), the chemical composition of capsules that consisted of sunflower oil, calcium-alginate, cement and epoxy resin was determined from the TGA test results analysis at 1000°C in N_2 atmosphere and the volumetric proportion between the shell and the core of the capsules was determined from the SEM images, as shown in Figure 2.29.

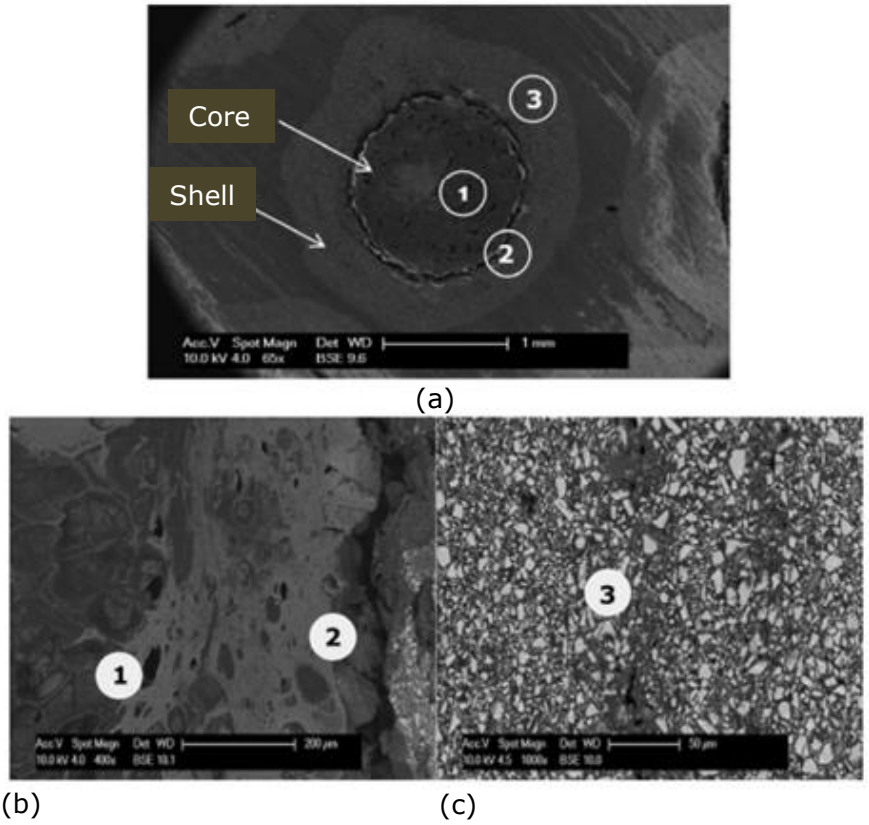

Figure 2.29 SEM images of capsule; (a) overview of the capsule; (b) zoom-in of the core and the core-shell interface; (c) zoom-in of the shell (Al-Mansoori et al., 2016).

2.10 Alginate as a material and as an encapsulations material

Alginate, is a naturally occurring linear anionic polysaccharide (Lotfipour et al., 2012). It is typically obtained from any of the six species of brown algae such as Laminaria japonica, Macrocystis pyrifera, Laminaria digitate, Laminaria hyperborean, Asco phylum nodosum, and Macrocystis pyrifera (Smidsrød and Skja., 1990; Clark et al., 1936).

During the extraction process, research shows that sodium chloride or Calcium chloride chemical additive is added to the filtrate in order to aid the precipitation of the alginate. Upon extraction, the alginate salt can be converted into the alginic acid by treating it with dilute hydrochloric acid (Smidsrød and Skja. 1990; Clark et al. 1936). A water-soluble sodium alginate powder is formed after further purification (Rinaudo, 2008). In Figure 2.30, the process of extracting sodium alginate is demonstrated.

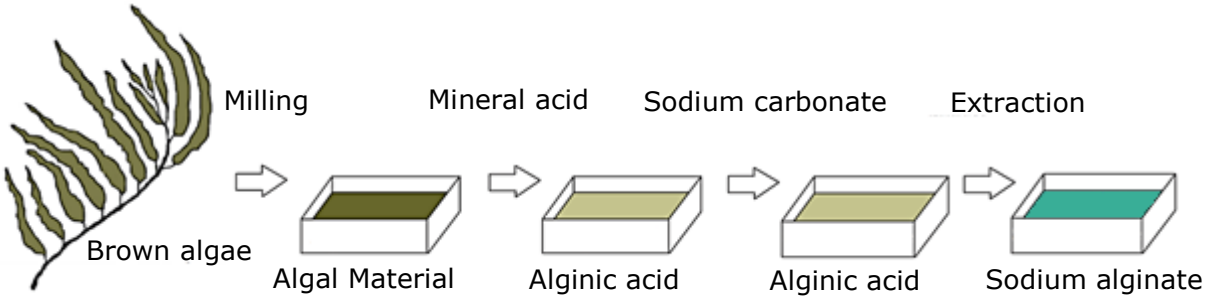

Figure 2.30 The procedure of sodium alginate extraction from brown algae (Sachan et al., 2009).

The alginate material can be formed into beads by appropriate mixing with calcium chloride solution. Figure 2.31 shows calcium chloride being dropped into the sodium alginate forming calcium-alginate beads.

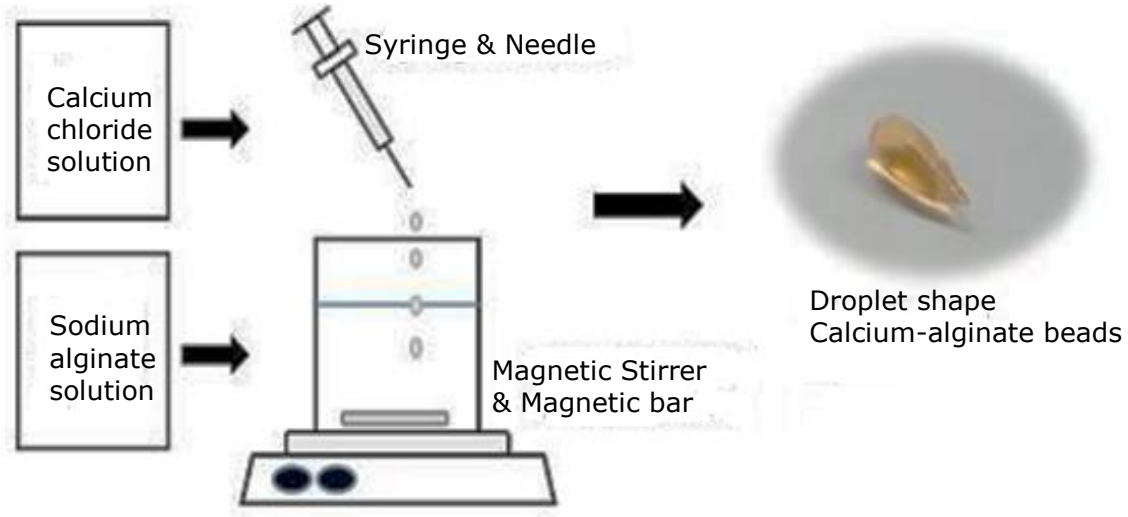

Figure 2.31 Encapsulation process of calcium-alginate beads (Sewiwat et al., 2016)

However, the most widely used method of formation of alginate beads/particles is one in which the alginate solution is dropped into the calcium chloride solution (Zuidam and Nedoviæ, 2010). Droplets of an aqueous solution of sodium alginate may be dripped into a calcium-chloride gelling bath using simple tools (Figure 2.32) such as a syringe, pipette, vibrating nozzle, spraying nozzle, jet cutter, atomising disk, coaxial air-flow, or electric field. The differences between some of encapsulation tools are stated below.

Jet Cutter

The jet cutter is located just beneath the nozzle where the jet is sliced into cylindrical pieces using a fast-rotating gadget made of pieces of wire (Pruesse at al., 2003). Once cut, the jet forms spherical-like beads/particles that fall into the calcium chloride solution and the resulting beads are collected.

Vibrating

Whenever the nozzle is vibrated, a wave known as a sinusoidal wave is produced which breaks up the liquid jet into small droplets, with one single drop formed per cycle (Nedovic and Willaert, 2013).

Rotating Disk Atomisation

This is a technique where the liquid is spread onto the rotating disk, and turned into a thin film by the centrifugal forces created by the rotating disk (Squier, 1973). Once the liquid acquires the correct velocity, it is relocated to the disk rim, where it is spread into small droplets that are dislodged from the disk to create a spray.

Coaxial Air-Flow

In coaxial air-flow, air is subjected to high pressure and used to spray both the core and wall material mixture that is poured from the top through the air atomiser orifice, from where it is channeled into the gelation bath (Garti and McClements, 2012).

Electrostatic Potential

This technique uses the differences in electric potential to pull the droplets from the tip of a needle (Mishra, 2015). It is noted that the capsule size may be monitored and controlled easily by simply adjusting the voltage size. In this respect, the higher the voltage used, the higher the electric force that is generated to pull the droplets. Consequently, it results in the production of smaller droplets and, hence, capsules.

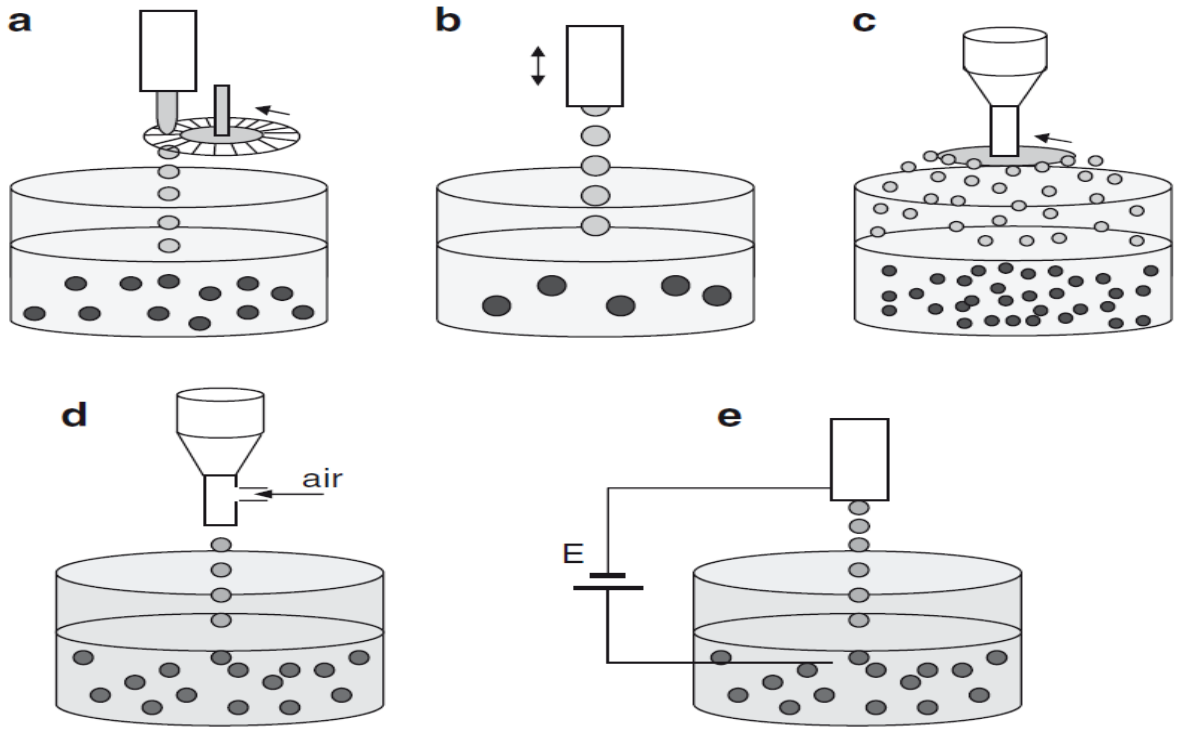

Figure 2.32 Set-ups of five different ways of making microspheres: (a) Jet Cutter , (b) pipette or vibrating nozzle (c), atomizing disk (d), coaxial air-flow (e) electrostatic potential (Zuidam and Nedoviæ, 2010).

2.11 Characterisation and Structure of Alginate

According to Myrnes (2016), alginate is an uronic acid with a hydroxyl group (-OH) and six carbons (C6). The hydroxyl group is oxidized to form a carboxyl-group (-COO-). In molecular terms, alginate belongs to a polymeric group that is made of two monomers (Guluronate (G) and Mannuronate (M)) that are linked by 1-4 glycosidic bonds. The blocks

are made up of consecutive G residues (GGGG) and consecutive M residues (MMM) as well as having alternating M and G residues (MGM), See Figure 2.33. The G blocks constitute between 25 to 75 per cent of the content (Simensen et al. 2000).

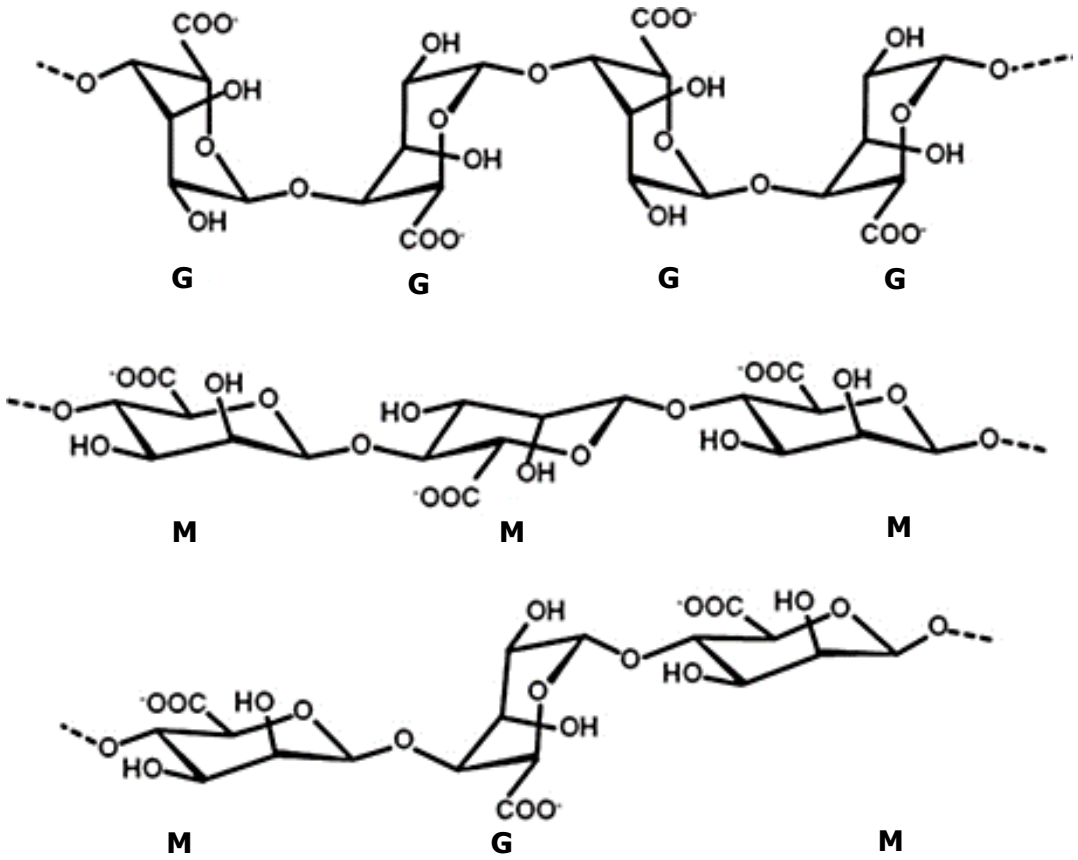

Figure 2.33 Chemical structures of G, M and alternating blocks in alginate (Lee and Mooney, 2012).

2.12 Properties of Alginate

Alginate is a biopolymer used in a variety of biomedical applications because it has unique properties, such as non-toxicity and biocompatibility (Aderibigbe and Buyana, 2018). It occurs naturally as a linear anionic polysaccharide extracted from brown seaweed (Sime, 1990). The brown algae have unique chemical and physical properties (Chaudhari et al., 2015).

Chemical properties of alginate: Van den Brink et al. (2009), stated that the chemical properties, especially the solubility of the alginate, is determined by free calcium

concentration, the total ionic solution strength, and the pH of the solvent. As shown in Figure 2.30, the conversion of alginic acid to the sodium alginate enhances the solubility of the alginate in cold and hot water (Abo-El-Enein et al., 2017).

Physical properties of alginate: The physical properties of alginate improve with molecular weight (Lee and Mooney 2012). An alginate solution formed from a polymer that has a high molecular weight is highly viscous. The viscosity of alginate solution increases as the molecular weight increases thereby making it hard to dissolve a highly concentrated alginate in any given amount of water (Da Silva et al. 2017). The commercially available sodium alginates have weight ranges from 32,000 to 400,000 g/mol. Furthermore, the pH of the solvent affects the viscosity of alginate solutions. The viscosity increases with a decrease in the pH. At a pH value of between 3 and 3.5, the viscosity reaches the maximum point because the carboxylate groups in the alginate backbone are protonated and form hydrogen bonds (Lee and Mooney 2012). Temperature is another element that affects the viscosity of alginate solutions. The increase in temperature causes a corresponding decrease in viscosity, at a rate of 2.5% per degree Celsius. The viscosity of alginate solution drops significantly during heating, it is therefore important to heat the solution during the dissolution process.

Da Silva et al. (2015) stated that the physical properties of the alginate solution are influenced by the preparation method of the alginate particles. The alginate particles are formed through extrusion of the alginate solution through a needle drop-wise in a bath of cations, such as in a calcium chloride solution (Paques 2014). The divalent cations bond solely to the guluronate blocks in the alginate chains because the structure of the guluronate blocks allows high-level coordination between the divalent ions (Lee and Mooney, 2012). The guluronate blocks of one polymer then form junctions with the adjacent polymer chains in the egg-box structure of cross-linking (Figure 2.34). It is important to note that at lower temperatures, the reactivity of ionic cross-linkers such as calcium ions is reduced, and cross-linking becomes slower.

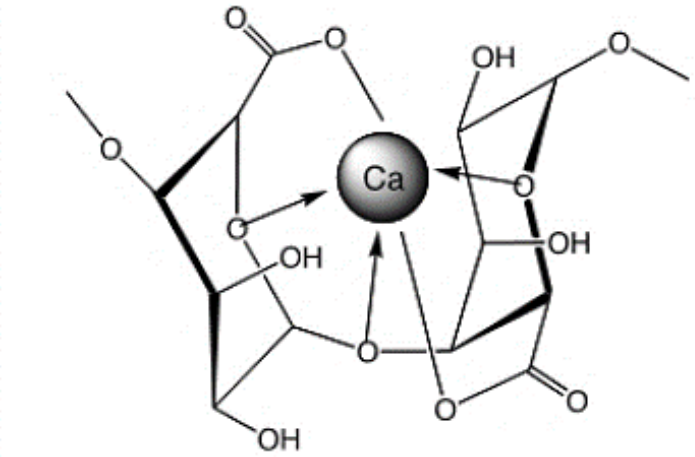

Figure 2.34 Egg-Box structure of calcium alginate structure (Inoue et al., 2018).

2.13 Variants of Alginate

In biomedicine applications, alginate is converted into a hydrogel (Lee and Mooney 2012). It is used in treating of wounds, as a tissue engineer, as well as in drug delivery. Hydrogels are high in water content. The hydrogels are formed through chemical and physical cross-linking of the hydrophilic polymers. The physiochemical properties of hydrogels are dependent on the cross-linking type and density, in addition to the chemical composition and molecular weight of the polymers (Lee and Yuk 2007; Varghese and Eliseeff 2006).

The water retention as shown in Table 2.4 by the calcium alginate is as high as 9.9 times more than their initial weight. However, the alginate retention of saline solution is less. Since the saline is identical to the serum found in wounds, it is considered as a better indicator of absorbency in a natural wound environment. The reduction in absorbency and retention is caused by the availability of salts in the saline solution.

Another example by Huang and Yang (2010) displays a water retention of both alginate-calcium chloride (AC) and alginate-calcium-Poly(glutamic acid) (AG), see Figure 2.35. The results of the study showed that the water retention of AG was higher than that of AC. The reason that AG exhibited the highest water retention is due to the presence of glutamic acid.

Table 2.4 Comparative physical properties of Alginate and Alchite fibre (Miraftab et al., 2010).

Fibre	Draw Ratio	Coagulation Bath	Fibre Diameter (μm)	Linear Density (dtex)	Water Retention [g/g]	Saline Retention [g/g]	Fibre Diameter Swell ratio
Alginate	1.15	1.00% CaCl2 solution	36.5	6.1	9.9	6.5	1.6
Alginate	1.23	1.00% CaCl2 solution	30.0	5.6	9.7	7.1	1.4
Alginate	1.31	1.00% CaCl2 solution	30.0	5.2	4.3	6.1	1.6

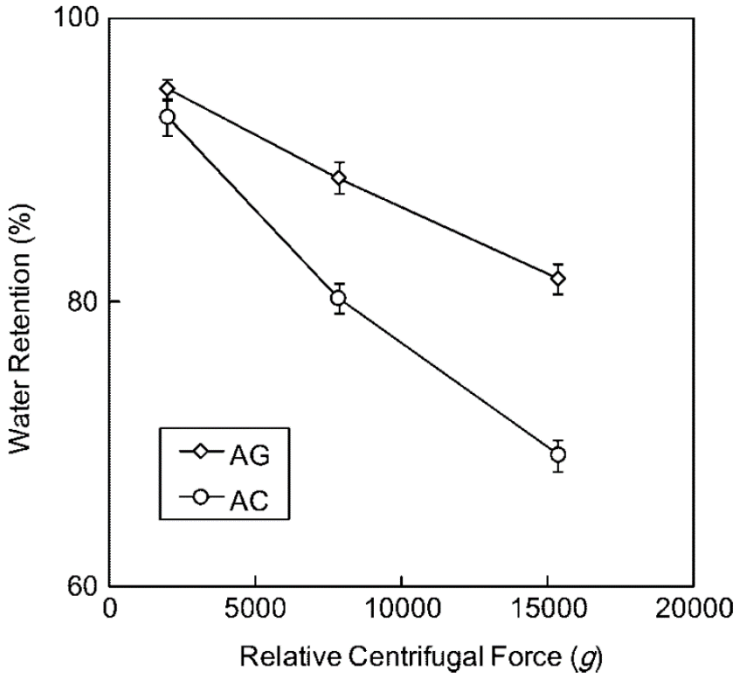

Figure 2.35 The water retention of alginate hydrogels (Huang and Yang, 2010).

2.14 Summary

When CMA is used, more than 95% of the energy required during the production of HMA can be saved. In general, CMA is prepared at ambient temperature and it consists of aggregates and bitumen emulsion. The bitumen emulsions typically consist of 40-75% bitumen, 0.1-2.5% emulsifier, and 25-60% water. Therefore, bitumen emulsion has to revert to bitumen so as to act as binder, and this process is known as emulsification or

breaking. However, a number of studies have reported that full curing may not take place until 2 to 24 months in the field. In addition, CMA includes high air void content, which can facilitate water damage and weak early life strength.

Several studies have contributed to evaluating the performance of CMA by using a laboratory compaction method as well as different additives, mainly those consisting of OPC materials under different curing protocols. In short, the studies confirm that the stiffness modulus of CMA increases when the degree of gyratory compaction increases.

Studies have confirmed that the stiffness of CMA increases with the curing time, but that, without additives such as cement, CMA cannot achieve the level of stiffness that hot mix can. Also, studies have confirmed that increasing the amount of OPC materials can improve the mechanical properties of CMA more than HMA with an increasing curing time. However, 1-2% rapid-hardening cement increases the strength more than the same amount of OPC (Thanaya, 2003). In addition, Fang et al. (2016) argued that the increase in the early strength of CMAs was attained not only due to the rapid-hardening cement but also due to the fact that they bind a higher amount of water than OPC.

Several, different, curing protocols of CMA have been proposed in the context of evaluating water damage in a laboratory. Studies have revealed bad cracks in CMA specimens without cement. Plain CMA specimens did not show any measurable stiffness modulus after soaking, while the CMA specimens with cement were found to exhibit approximately 1200 MPa which exceeded half the value obtained for un-soaked specimens. Al-Hdabi et al. (2014) and Al-Busaltan et al. (2012) established a water damage protocol involving 3-days soaking at 40°C. The water damage protocol was applied prior to 7 days of curing the specimens, because the specimens of the control mix showed very low strength at early age.

Furthermore, several studies have shown alginate as a material and as an encapsulation material. This alginate material can be formed in particles/beads by mixing with calcium-chloride solution (Sewiwat et al., 2016). The alginate particles can be formed through

extrusion method. As the study reported in this thesis aims to investigate the performance of a new cold mix asphalt (CMA) made with bitumen emulsion capsules, alternative encapsulation techniques have been investigated. Several different methods such as spray drying, spray cooling, coacervation, lyophilisation, Pickering emulsion and extrusion are available. The extrusion method has been widely used in fields such as food industry, industrial ceramics, and electronic components. Moreover, this extrusion method can be carried out with simple tools such as a syringe, pipette, vibrating nozzle, spraying nozzle, jet cutter, atomising disk, and coaxial airflow, or an electric field making it ideal for this study. Furthermore, the particle sizes produced by this method fall within the range of 300-5000μm, which may be suitable for mixing with the aggregate particles. Therefore it was decided to use the extrusion method in this project.

The study will also investigate the use of Ca-alginate capsules containing no bitumen emulsion. This will help to demonstrate the relative effect of the bitumen and the alginate itself.

Chapter 3: Cold Mix Pavement Material made with Calcium-Alginate

3.1 Introduction

Cold Mix Asphalt (CMA) is a complex road construction material that is manufactured at ambient temperature by mixing aggregates with water and a bitumen emulsion (or foamed bitumen) that acts as the binder. In the United Kingdom, the use of CMA is largely limited to surface treatments, such as surface dressing and slurry surfacing, as well as bond/tack coating (Brown and Needham, 2000). The strength of CMA tends to be easily affected by the exposure to environmental and mechanical factors, such as moisture and continuous traffic loads (Marienfeld and Guram, 1999; Liang and Zhou, 1997). This happens because moisture reduces the curing rate of CMA and increases its damage susceptibility (Choudhary et al., 2012) by effect of the loss of the interfacial adhesion properties of the mixture (Guo et al., 2014). Authors such as Thanaya et al. (2009) and Khalid and Mooney (2009) have reported that CMA presents some disadvantages compared with conventional Hot Mix Asphalt (HMA), such as high air void content, weak life strength, and long curing times. Nevertheless, CMA also presents advantages in terms of costs, ecology, energy savings and health and safety performance compared with conventional hot mix asphalts (Saadoon et al., 2017). Likewise, the flexible performance of CMA makes them especially attractive for low-medium traffic roads (Gómez-Meijide and Pérez, 2014). Some weaknesses of CMA versus hot mixes are principally as a result of their design variables and manufacturing conditions.

In CMA manufacturing, the bitumen emulsion must be reverted into bitumen to act as a binder: a process known as de-emulsification or breaking (Das, 2008; Saadoon et al., 2017). Water inside the CMAs is the main factor that delays their strength gain (Oke, 2011). Water is the second element of bitumen emulsions and comprises between 25% and 60% of an emulsion (James, 2006). The curing of CMAs is a process where water

evaporates from CMA and the bitumen can bind the aggregates together (Saadoon et al., 2017). CMAs thereby gain strength with the curing time (Fang et al. 2015). Previous studies have reported that full curing of the cold mixes by effect of the interstitial water evaporation may take place between 2 to 24 months under field conditions (Thanaya, 2007). Hence, it is very important to remove the water from emulsions of CMA to improve the strength and accelerate the curing time (Fortuny et al., 2007; Jenkins, 2000; Saadoon et al., 2017).

Additionally, to accelerate cold mix asphalt curing and improve its mechanical properties, lime or Portland cement can be added to the mixture (Oruc et al., 2006; Fang et al., 2015). Cement provides improvements to Marshall stability (Wang and Sha, 2010), lower moisture content, curing rates, enhanced strength and material stiffness, and improves the compatibility of the aggregates with the emulsion (Fang et al., 2015). For these reasons, between 1% and 3 % of Portland cement may be added to cold mixes by mass of aggregates (Head, 1974; Thanaya, 2007).

This chapter describes the preparation of Cold Mix pavement Materials made with calcium-alginate Capsules (CMC) or Particles (CMP) as an alternative material to conventional Cold Mix Asphalt (CMA). To do that, bitumen emulsion has been encapsulated in a calcium-alginate matrix and, calcium-alginate particles have been manufactured. The capsules and particles were then mixed with aggregates and compacted, it was found that they created a composite material that is stronger than standard CMA. In the chapter, the influence of the amount of calcium-alginate capsules and particles is evaluated. Furthermore, the effect of compaction energy, curing time and cement additions on the mechanical properties of CMC and CMP is evaluated.

3.2 Materials and Methods

3.2.1 Raw Materials

Limestone aggregates, bitumen emulsion, Portland cement and bitumen were used in this study. Raw materials for calcium-alginate capsules and particles consisted of a cationic bitumen emulsion K1-60, 60% bitumen content, with density of 1.03g/cm^3, sodium alginate ($C_6H_7O_6Na$) and, calcium chloride ($CaCl_2$) in granular pellets and 93% purity. The aggregates used were well-graded crushed limestone, with size between 14mm and a few microns (see the aggregate gradation in Figure 3.1), aiming at a dense mix following a further carve, see Appendix B. Portland cement type CEM I 52.5 N was used as a filler replacement to improve the properties of CMC. Finally, virgin bitumen of 160/220 penetration grade was used to manufacture hot mix asphalt for comparison purposes, matching the penetration of the bitumen in the emulsion.

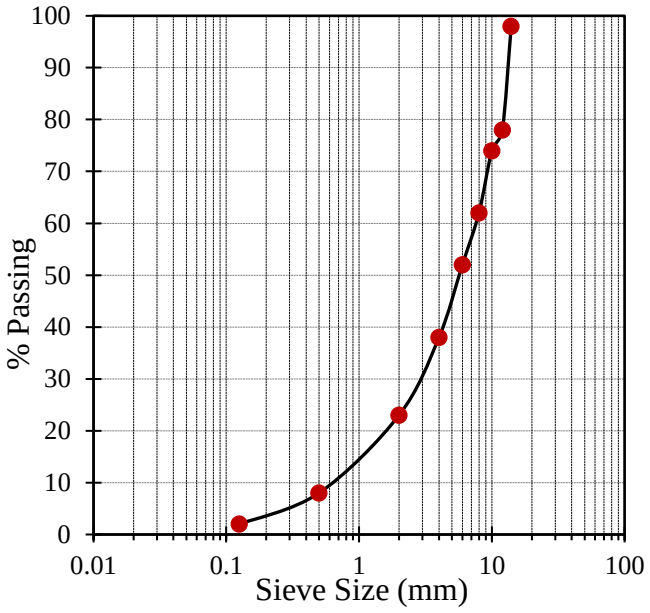

Figure 3.1 Aggregate size distribution used in the mixture studied.

3.2.2 Encapsulation Procedure of calcium-alginate capsules and particles

The calcium-alginate capsules were prepared by ionotropic gelation of alginate in the presence of calcium. Figure 3.2 shows a schematic diagram of the preparation of the

capsules.

The encapsulation procedure used in this chapter is as follows:

- First, 800ml of bitumen emulsion, 100g of sodium alginate and 1200ml of deionised water were pre-heated at 95ºC, introduced into a 2500ml Pyrex glass container that was on a hot plate to maintain the temperature at 95ºC and stirred at 6000rpm for 15min until a stable bitumen-alginate emulsion was produced.

- At the same time, a calcium chloride solution was prepared by mixing 250ml of deionised water with 15g of calcium chloride in a 500ml Pyrex glass container that was on a hot plate prepared to maintain the solution at 95ºC and, stirred at 400rpm for 15min to produce a stable calcium chloride solution.

- Then, the calcium chloride solution at 95ºC was placed into a blender device and stirred at 13600rpm for 1min. Capsules were produced by letting the bitumen-alginate emulsion drop into the calcium chloride solution from a 1000ml pressure equalising dropping funnel (at an approximate speed of 1.7mm/min) with a 3mm outlet size, the blades in the blender cut the drops before the calcium-alginate had hardened, producing capsules of approximately 0.5 mm diameter. The bitumen emulsion was encapsulated into a polymeric porous structure by the cross-linking of calcium-alginate via ionotropic gelation of sodium alginate in the presence of calcium ions. Al-Mansoori et al (2017) and Norambuena-Contreras et al (2018) have used this encapsulation technique with successful results to produce calcium-alginate (Ca-alginate) capsules with asphalt for self-healing purposes.

- After this, the capsules were left in the calcium chloride solution for 24h, to reduce their temperature to 20±1ºC. Then, the capsules were sieved and washed with deionised water. They were dried for 30min under the constant movement of air at 20±1ºC, produced by a fan. Finally, the Ca-alginate capsules containing bitumen emulsion were stored in a freezer, at -20ºC to minimise any possible degradation.

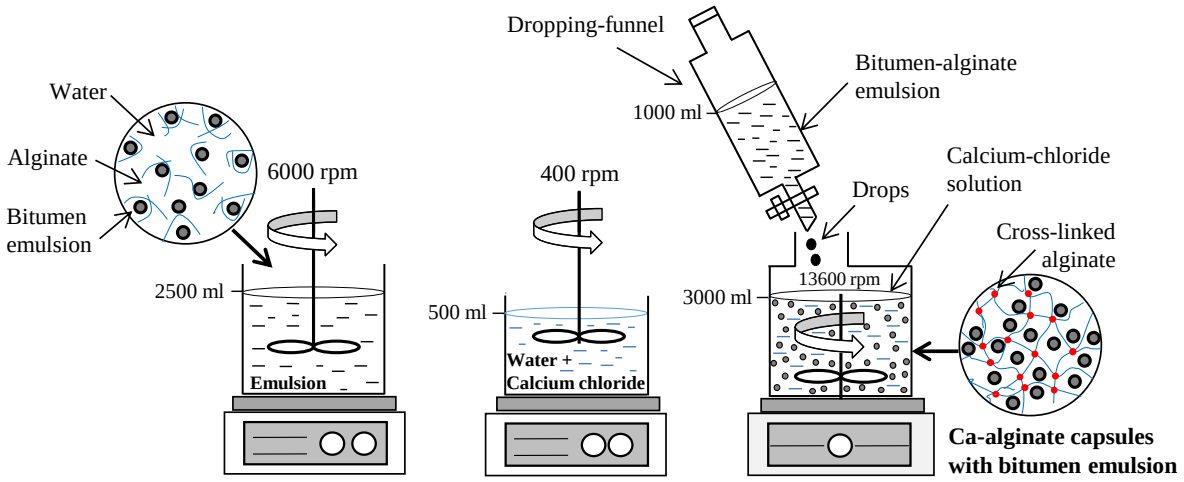

Figure 3.2 Schematic diagram of the preparation of Ca-alginate capsules containing bitumen emulsion. The procedure is also applicable to the manufacturing of the Ca-alginate particles without bitumen emulsion.

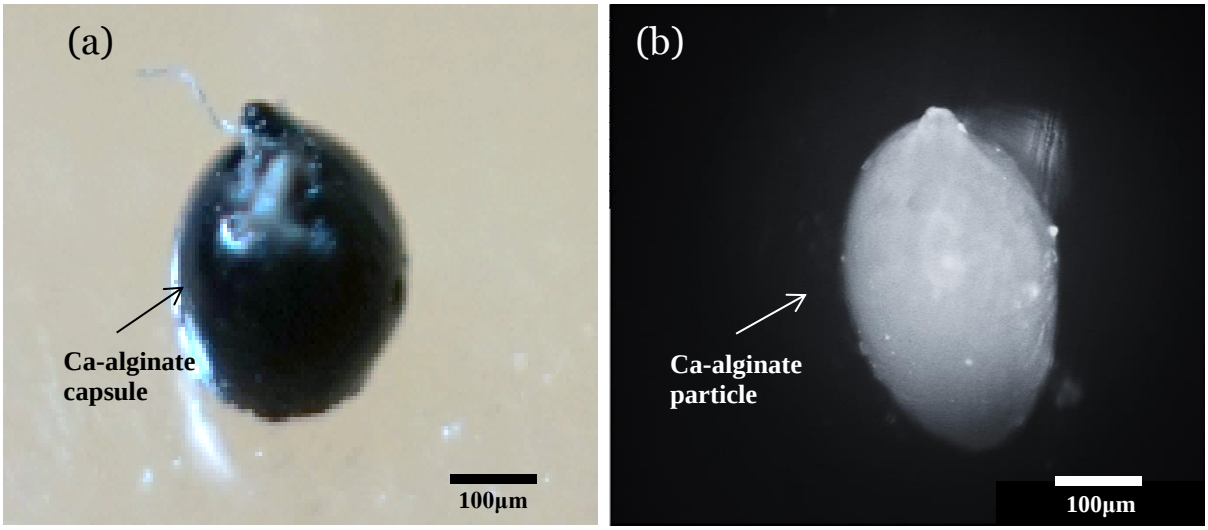

Figure 3.3 (a) Optical image of an individual Ca-alginate capsule containing bitumen emulsion. (b) Fluorescence image of an individual Ca-alginate particle without bitumen emulsion.

Furthermore, the same proportions of calcium-chloride, sodium alginate, water and the same experimental procedure were selected to manufacture Ca-alginate particles, which did not contain bitumen emulsion. These particles were made with the intention of evaluating the binding effect of bitumen emulsion. Examples of an individual calcium-

alginate capsule that contains bitumen emulsion and a calcium-alginate particle without bitumen emulsion are shown in Figure 3.3(a) and (b), respectively.

3.2.3 Test Specimens Preparation

A preliminary investigation of different compaction techniques such as Marshall, gyratory and vibratory compaction were used in this study. The Marshall compaction is almost certainly better than other compaction techniques used in this study and for more details, see Appendix A. Therefore, Marshall test specimens with 100 mm diameter and 50 mm height were prepared (see Figure 3.4). Table 3.1 describes the manufacturing process for the 15 different types of mixture evaluated in the study. The raw materials used in the preparation of the mixtures such as bitumen, bitumen emulsion, calcium-alginate capsules and calcium-alginate particles with, and without, cement addition, were manufactured in batches with 3060 g of aggregates. The amount of raw materials in the mixture was added by total weight of aggregates, see percentages in Table 3.1.

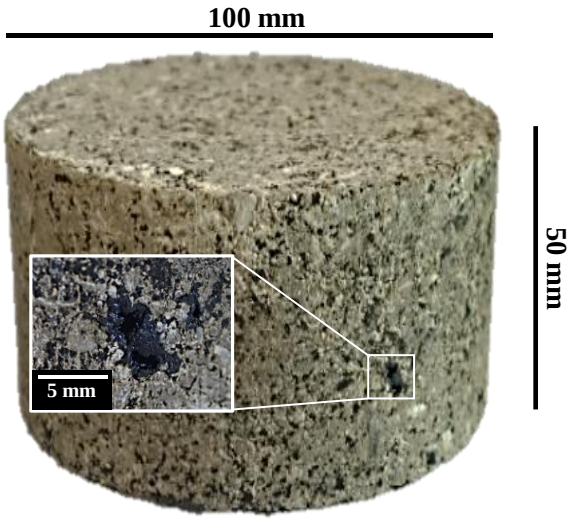

Figure 3.4 Test specimen of cold mix pavement made with Ca-alginate with bitumen emulsion.

Table 3.1 Composition and manufacturing process used for the mixtures studied.

Mixture type	Manufacturing process description	Abbreviation	Purpose
Hot Mix Asphalt	Raw materials were pre-heated at 160ºC for 2h. Then, aggregates with 3% of bitumen were mixed in a planetary mixer for 2 min at 160ºC and poured into the Marshall moulds. The mixtures were compacted at 140ºC applying 50 blows on each flat face.	HMA	Reference Material.
Cold Mix pavement material made with calcium-alginate Capsules (see Figure 3(a)) that contain bitumen emulsion (CMC)	Aggregates, 4% or 10% w/w of calcium-alginate capsules (%Cap: 4, or 10, respectively) and 0%, 1%, 2% or 3% of cement (%Cem: C0, C1, C2 and C3, respectively) were mixed for 2 min at 20±1ºC, followed by 60s of mixing by hand. Then, the mixture was poured into Marshall moulds and compacted by applying 20, 40, 50, 70, 80 or 100 blows (N_{Blows}: 20, 40, 50, 70, 80, 100, respectively) on each flat face of the specimens.	CMC %Cap %Cem - N_{Blows} *e.g. CMC 4C1-50 means that 4% w/w of capsules were used, 1% w/w of cement was added and, 50 blows were applied to compact the mixture.*	Novel mix to investigate use of capsules to deliver emulsion more uniformly.
Cold Mix pavement material made with calcium-alginate Particles (see Figure 3(b)) (CMP)	Aggregates with 4% or 10% of calcium-alginate particles (%Par: 4, or 10, respectively) were mixed for 2 min at 20±1ºC, followed by 60s of mixing by hand. After this, the mix was poured into the Marshall moulds and compacted always by applying 50 blows on each flat face.	CMP %Par %Cem - N_{Blows} *e.g. CMP 4C0-50 means that 4% w/w of calcium-alginate particles were used, 0% w/w of cement was added and, 50 blows were applied to compact the mixture.*	Mix added to distinguish contribution of alginate alone.
Cold Mix Asphalt (CMA)	150 ml of water and aggregates were mixed for 1 min at 20±1ºC. Then, 7% or 17% w/w of bitumen emulsion (%E: 7, 17) and 0% or 1% of cement (%Cem: C0 and C1, respectively) were mixed for 3 min followed by 60s of mixing by hand. After, the mixes were poured into Marshall moulds and compacted always by applying 50 blows (N_{Blows}: 50) on each flat face of the specimens.	CMA %E %Cem - N_{Blows} *e.g. CMA 7C1-50 means that 7% of bitumen emulsion and 1% w/w of cement were used and, 50 blows were applied to compact the mixture.*	Conventional CMA for comparison of performance.

The 3% of bitumen in the HMA mix, as shown in Table 3.1 was chosen based on a previous study conducted by Al-Sayed et al. (1995). The aim was to obtain a HMA material with comparable stiffness and strength to that of the CMA with 7% w/w bitumen emulsion (although, in fact, it was somewhat more competent as later chapters reveal). Additionally, The 4% and 10% of particles or capsules in the CMP or CMC mixes, as shown in Table 3.1 were selected to be compared with the approximately 4% and 10% of residual bitumen in the CMA.

3.2.4 Morphological Characterisation of the Calcium-alginate Capsules and Particles

The morphology of the Ca-alginate capsules and particles was evaluated by Optical microscopy, Fluorescence microscopy and Environmental Scanning Electron Microscopy (ESEM). To determine the size distributions of the capsules and particles, more than 120 capsules and particles were randomly selected and examined by using a stereo microscope at 5 and 20 magnification. The ESEM scanner of samples containing Ca-alginate capsules and particles was also carried out.

3.2.5 Water Content of the Calcium-alginate Capsules and Particles

To measure the accessible water content in the calcium-alginate capsules and particles, 3 samples of approximately 50g of each type were dried in an environmental room with constant movement of air, at 20±1ºC for 24h. After 24h, the capsule and particle samples were dried using a silica desiccant for 8h, and then weighed using a precision balance.

3.2.6 Density of the Calcium-alginate and Particles

To determine the density of the calcium-alginate capsules and particles, a Helium Pycnometer was used. It was chosen because it has the ability to measure the real density of a granular or porous solid by determining the volume of the solid portion isolated. The test was carried out at room temperature 20±1ºC, and 3 samples of approximately 0.2g of each capsule and particle type were poured into a sealed sample chamber size $1cm^3$

within the pycnometer. Finally, the density of calcium-alginate capsules and particles was recorded at 20min at a pressure value of 165kPa.

3.2.7 Marshall Stability test

The Marshall Stability test was used in this study to measure the mechanical performance of the pavement materials studied. The tests were executed according to BS EN 12697-34, at 20±1ºC, and the loading speed rate applied in the specimens was 50mm/min. The test temperature was chosen based on previous study conducted by Garcia et al. (2013). In the case of the hot mix asphalt, the specimens were immersed in a water bath at 60ºC for 40 minutes before testing, and the elapsed time between the removal of the specimens from the water bath to the test did not exceed 30 seconds. The Marshall results shown are the average of 3 tests.

3.2.8 Curing Process of the test Specimens

All the Marshall test specimens of the CMA, CMC, and CMP materials studied (see Table 3.1) were demoulded after compaction, and cured at room temperature, 20±1ºC and relative humidity of 60% for six different curing times: 1, 3, 7, 14, 21 and 28 days (Garcia et al. 2013; Gómez-Meijide and Pérez, 2014).

3.2.9 Water Content in the test Specimens at Different Curing times

Water content in the Marshall test specimens was measured following the procedure described by Garcia et al. (2013). For that, the mass of each test specimen at the different curing times (from 1 to 28 days) was recorded using a balance with a precision of 0.5g. Then, after 28 days, the same test specimens were dried at 90ºC for 12h and weighed again to determine the remaining amount of water in the mixture and the water content of each sample was calculated by the following equation:

$$WC_m = \left(\frac{m_{ct_i} - m_{dry}}{m_{dry}}\right) \times 100 \qquad (1)$$

Where m_{cti} is the mass in (g) of the test specimen at a specific curing time *i*, and m_{dry} is the mass in (g) of the same test specimen after 28 days and dried at 90ºC for a period of 12 h.

3.2.10 X-ray Computed Tomography

X-ray computed tomography (CT-Scan) was used to evaluate and compare the air voids distribution in 50mm length and 50mm width test samples of CMC 4C2-50 that had been cured for 1 day, and HMA. For CT-Scan characterization, a micro CT system operated at 160kV and 63μA with a pixel size 55μm was used. Additionally, a small sub-sample of approximately 5 mm long taken from the CMC 4C2-50 sample was also examined. The micro CT system operated at 60kV and 83μA with a pixel size of 5.7μm was also used.

3.3 Results and Discussion

3.3.1 Evaluation of the Morphology and Composition of the Capsules and Particles

Based on the optical microscopy measurements, it was found that the size of the Ca-alginate capsules and particles exhibited a normal distribution curve with the majority of agglomeration diameters ranging from 0.4mm to 0.64mm for capsules, Figure 3.5(a), and from 0.4mm to 0.74mm for particles, Figure 3.5(b).

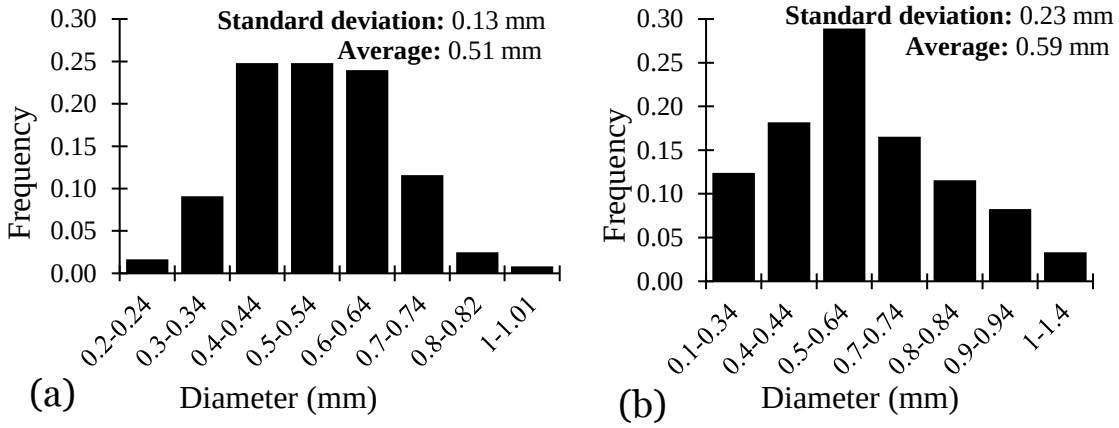

Figure 3.5 Sizes distribution of: (a) Ca-alginate capsules, see Figure 3(a), and (b) Ca-alginate particles, see Figure 3(b).

By knowing that the average water content was approximately 67% in the capsules and 73% in the particles (meeting the expectation of high water content refer to Section 2.13), the density of the capsules was 1.12g/cm^3, the density of the bitumen emulsion was assumed to be 1.03g/cm^3, and the density of the calcium-alginate polymer was 1.74 g/cm^3, the composition of Ca-alginate particles can be readily calculated and the composition of Ca-alginate capsules can be assessed by using the following two equation system:

$$\begin{gathered} M_b + 67 + M_p = 100 \\ \rho_{b-cap} \times \left(\frac{M_b}{\rho_b} + 67 + \frac{M_p}{\rho_p} \right) = 100 \end{gathered} \quad (2)$$

where M_b and M_p are the mass proportions, expressed as percentages of bitumen emulsion and calcium-alginate, respectively; $\rho_{b\text{-}cap}$ is the density of the capsules; ρ_b is the density of the bitumen emulsion; and ρ_p is the density of the calcium-alginate polymer.

Table 3.2 presents the composition for the Ca-alginate capsules and particles.

Table 3.2 Components of the calcium-alginate capsules and particles.

Binder type	Percentage (%) in mass of the raw materials		
	Bitumen emulsion	Water	Calcium-alginate
Capsules (see Figure 3(a))	8	67	25
Particles (see Figure 3(b))	-	73	27

3.3.2 Effect of Compaction and Cement addition on the Mechanical Strength of CMC

Figure 3.6 shows the average Marshall force resisted by CMC specimens made with capsules and 3 different cement contents, after 24h curing, at 20ºC. In every case, the force resisted increased approximately linearly with the number of blows applied; e.g., in the CMC 4C0 mixtures, from 2.21kN at 20 blows to 9.22kN at 100 blows. Moreover, the force resisted by the CMC increased approximately proportionally to the amount of cement addition. For instance, in the CMC with 0%, 1%, 2% and 3% of cement the slopes were 0.08kN/blow, 0.12kN/blow, 0.17kN/blow and 0.21kN/blow, respectively. It is unclear if

the strength increase caused by cement is mainly due to the hydration properties of the cement or to the interaction of the cement's hydration product and calcium-alginate. Further research is still required to understand this more fully.

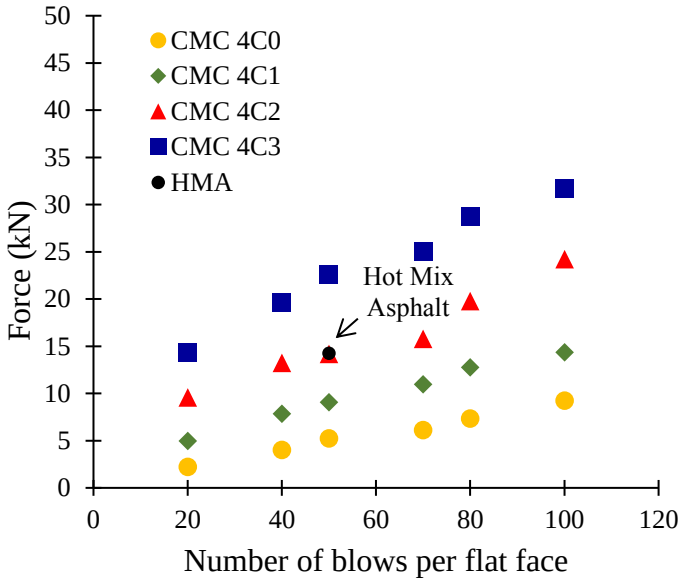

Figure 3.6 Variations in the Marshall force resisted by CMC test specimens, after 24h curing at 20°C due to the effect of Marshall compaction configurations and Portland cement additions.

Additionally, the average strength registered for HMA, compacted with 50 blows per flat face, is also shown in Figure 3.6. For the same number of compaction blows, the average force resisted by the HMA specimens was similar to that of CMC 4C2-50. Note that although the testing temperature of HMA was 60ºC while CMC 4C2-50 was tested at 20ºC, later chapter will revealed that the material is indeed of similar competency to HMA.

Moreover, Figure 3.7 shows the average air void distribution across the height of CMC 4C2-50 and HMA samples, measured from CT-Scan images. It can be observed that the air void contents across both test samples (line A-A') were approximately 7.2% and 7.6%, respectively. CMC shows very similar strength and air void content to HMA after 24h curing, which may be due to the interaction of the cement's hydration products with the Ca-alginate capsules' materials, although further research is still required to understand the reasons for this.

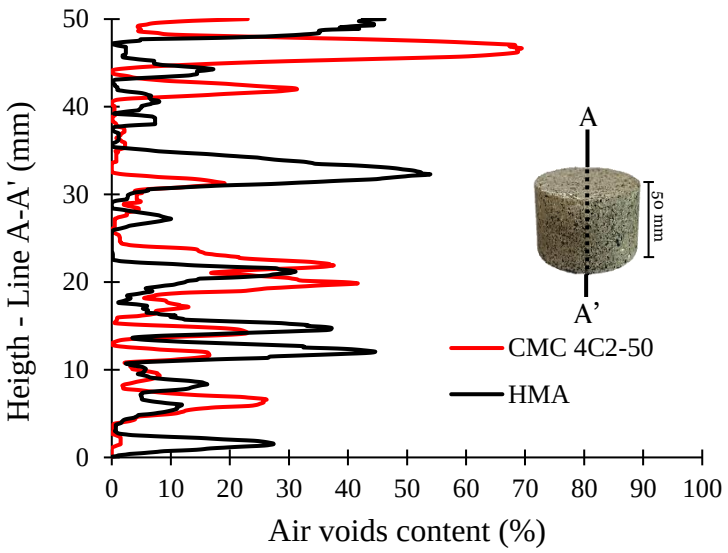

Figure 3.7 Air voids distribution along the vertical axis of CMC 4C2-50 and HMA test samples.

Figure 3.8(a) shows an example of a CT-Scan cross-section image of the internal microstructure of CMC 4C2-50, after 24 hours curing. In this figure, it can be observed that, although the shape of the capsules has adapted to the solid skeleton of the material, the bitumen in the capsules remained unmixed. Furthermore, most of the bitumen emulsion in the capsules, remained unmixed and unbonded to the aggregates. This, and the low amount of bitumen used in CMC are indications that bitumen is not the main bonding material in CMC. Moreover, a dense binder can be observed between the particles, which may be composed of cement and calcium-alginate. It is important to comment on the existence of inorganic-organic composite building materials, composed of sticky rice and lime, which were used in ancient China as a binder in public constructions, such as roads, or walls (Yang et al., 2010). The inorganic component was calcium carbonate, and the organic component was amylopectin, which comes from the sticky rice soup added to the mortar and works by combining chemically with the lime and inhibiting the growth of calcium carbonate crystals, which produced a very compact microstructure. This material had lower water absorption properties, higher strength, and lower shrinkage than lime used on its own (Luo and Zhang, 2013). The authors hypothesize that unreacted alginate remained in the capsules and alginate may have reacted with the cementitious materials

to produce a binder that is equivalent to that reported by Yang et al. (2010) and Luo and Zhang (2013) between sticky rice, which has a similar composition to that of alginate, see Sachan et al. (2010), and lime. This remains to be investigated.

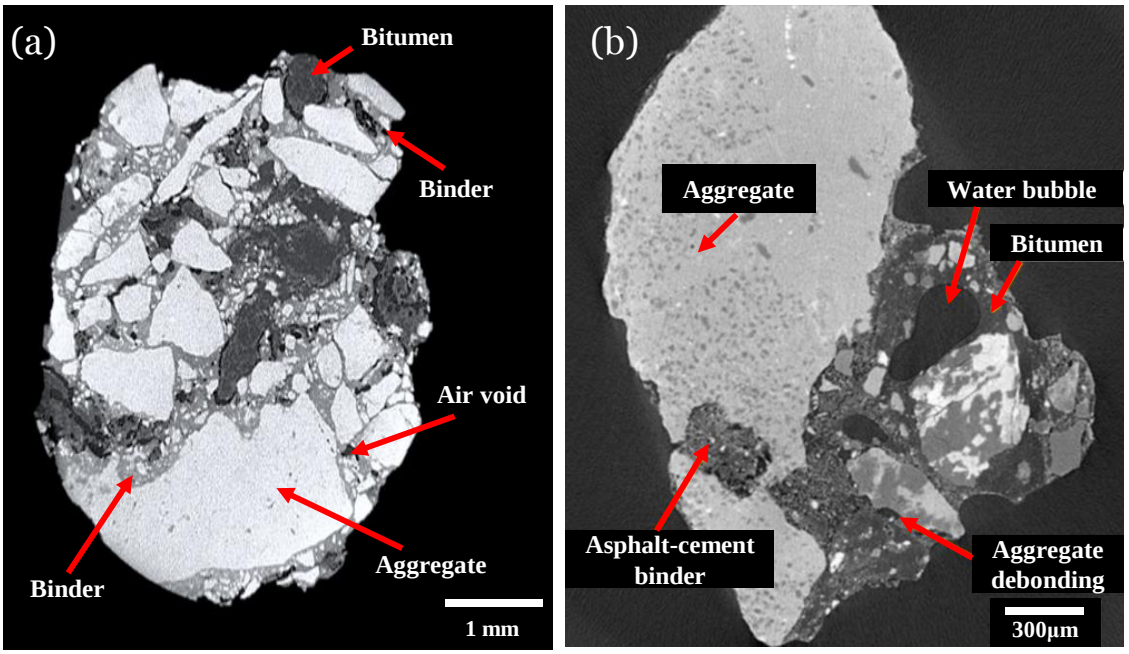

Figure 3.8 (a) CT-Scan detail of a cold mix pavement material sample CMC 4C2-50, cured for 28 days. (b) CT-Scan detail of a CMA, taken from a test sample, cured for 28 days, with 6% of cement (modified from Garcia et al. 2013).

Finally, by comparing Figure 3.8(a) to Figure 3.8(b), the latter corresponding to a CMA with 6% of cement (reported in Garcia et al., 2013), it can be observed that CMC shows a much denser microstructure, which corresponds to a lower amount of water in the material and helps to explain its early strength acquisition.

3.3.3 Effect of Binder type and Amount on the Mechanical Strength of Cold Mixes at Different Curing Times

Figure 3.9(a) shows the average results of Marshall force registered at different curing times for CMA, CMC and CMP test specimens. All specimens have been compacted with 50 blows on each flat face. From Figure 3.9(a) it can be concluded that:

1) The strength of CMA, CMC and CMP specimens increased with the curing time, and

2) The strength resisted by all the materials depended on the type of binder used, i.e., bitumen emulsion, Ca-alginate capsules or particles and,

3) The strengths also depended on the amount of binder added to the mixtures. From these data, it is relevant to note that the mass percentage of bitumen contained in the CMC specimens with 4% and 10% of capsules was 0.20% and 0.50%, respectively. This represents amounts of 15 and 6 times less bitumen, than in HMA. Likewise, the amount of calcium-alginate contained in CMC made with 4% and 10% of capsules was 0.98% and 2.46%, respectively.

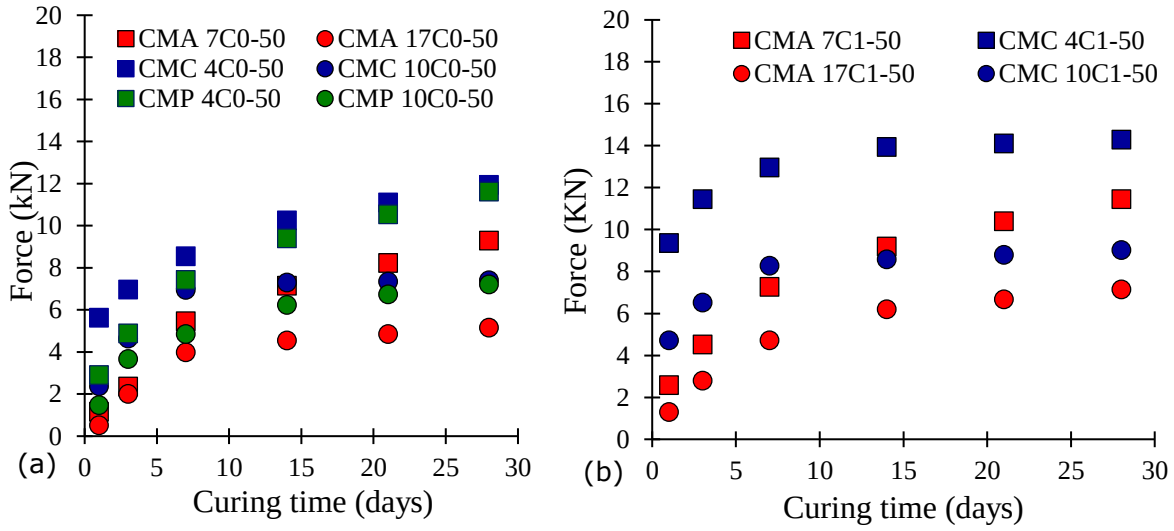

Figure 3.9 Marshall force registered at different curing times for (a) CMA, CMC and CMP without cement, and (b) CMA and CMC with 1% Portland cement.

In Figure 3.9(a) it can be observed that the force resisted by CMA 7C0-50 and CMA 17C0-50 at 1 and 28 days curing increased from 1.15kN to 9.29kN, and from 0.51kN to 5.15kN, respectively. This increase of the strength with time is consistent with the conclusions published by Saadoon et al. (2017) that indicated that CMA gained strength with the curing time due to the evaporation of water from the road's surface. The addition of bitumen emulsion introduces an excess of water in the mix, which delays the adhesion of bitumen to the aggregates and increases the required curing time. For example, the mixture with 17% bitumen emulsion (CMA 17C0-50) showed lower strength than the mixture with 7%

emulsion (CMA 7C0-50). This can be seen by comparing the results of average water content for both mixes, shown in Table 3.3 and Table 3.4 where it is observed that the water contents and air voids contents for CMA specimens with 17% of bitumen emulsion were always greater than these of specimens with 7% for all evaluated curing times. This effect also occurred in the cold mix specimens containing different amounts of Ca-alginate capsules (CMC) with bitumen emulsion and Ca-alginate particles (CMP), where higher contents of capsules, from 4% to 10%, did not increase the strength of the mixture, probably as a result of the increase in the water content of the test specimens, although this hypothesis must still be confirmed in further research.

Table 3.3 Water content in % w/w of the cold mix specimens measured at different curing time.

Mixture type	Curing time (days)					
	1	3	7	14	21	28
CMA 7C0-50	3.51	2.63	1.58	0.9	0.68	0.45
CMA 17C0-50	4.88	3.8	2.71	1.47	1.22	0.96
CMP 4C0-50	0.95	0.69	0.36	0.26	0.19	0.13
CMP 10C0-50	3.09	1.89	0.98	0.74	0.64	0.44
CMC 4C0-50	0.86	0.65	0.28	0.18	0.14	0.11
CMC 10C0-50	2.84	1.79	0.84	0.63	0.52	0.42
CMA 7C1-50	3.32	2.49	1.48	0.76	0.53	0.34
CMA 17C1-50	4.68	3.59	2.54	1.29	1.05	0.78
CMC 4C1-50	0.81	0.6	0.24	0.13	0.1	0.06
CMC 10C1-50	2.61	1.63	0.78	0.55	0.42	0.31

Table 3.4 Air voids content in % of the cold mix specimens measured at different curing time.

Mixture type	Curing time (days)					
	1	3	7	14	21	28
CMA 7C0-50	11.8	12.9	14.2	15.1	15.4	15.6
CMA 17C0-50	13.0	14.5	15.9	17.4	17.7	18.1
CMP 4C0-50	9.2	9.5	9.8	9.9	10.1	10.2
CMP 10C0-50	11.8	13.3	14.4	14.6	14.8	15.0
CMC 4C0-50	9.4	9.6	10.0	10.1	10.1	10.2
CMC 10C0-50	11.4	12.7	13.8	14.1	14.2	14.3
CMA 7C1-50	10.6	11.7	13.0	13.9	14.2	14.5
CMA 17C1-50	12.5	13.8	15.2	16.8	17.1	17.4
CMC 4C1-50	8.5	8.9	9.2	9.4	9.4	9.4
CMC 10C1-50	10.2	11.5	12.6	12.8	13.0	13.1

Figure 3.9(a) shows that CMC 4C0-50 and CMC 10C0-50, made with Ca-alginate capsules had higher strength than all the CMA test specimens evaluated in this figure. The different structures in Figure 3.10(a) and Figure 3.8(b) indicates the densities, with the different densities it shows different strength. Densities are shown in Table 3.5, for all curing times. Furthermore, the strength of CMP 4C0-50 and CMP 10C0-50 was remarkably similar to the strength of equivalent CMC materials, at every curing time, although approximately 5% lower. This result can be due to the bitumen in the capsules, which helped the bonding of the aggregates and therefore increased the mechanical strength of the mixtures. As an indication of this, in Figure 3.10(b), it can be observed that small globules of bitumen are well integrated within the binder. In addition, it can be observed that in mixtures with 4% of capsules, bitumen played an important role on the binding of the aggregates, especially during the first 14 days curing. Moreover, the fact that the Marshall force resisted by the material was lower with higher additions of binder, points to an optimum amount that must be studied in further research. Based on the previous results, it can be concluded that calcium-alginate was the main contributor to the increase of strength of the material and cold mixes made with capsules and particles and likewise Ca-alginate particles can be used as an excellent alternative as binder in cold mixes instead of bitumen emulsion.

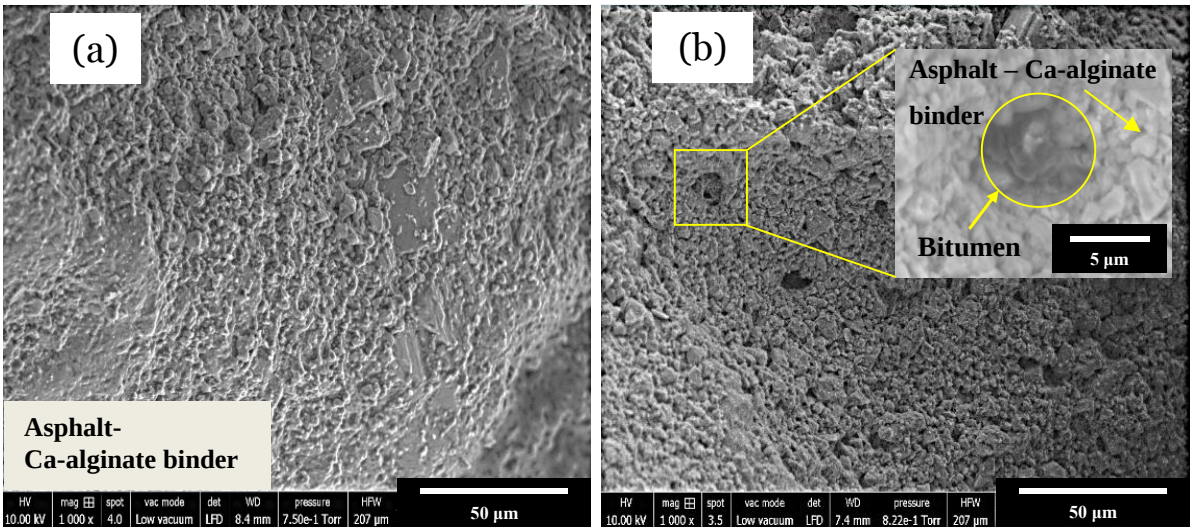

Figure 3.10 ESEM images of the binder's detail for mixes: (a) CMP 4C0-50 and, (b) CMC 4C1-50.

Table 3.5 Density in kg/m^3 of the cold mix specimens measured at different curing time.

Mixture type	Curing time (days)					
	1	3	7	14	21	28
CMA 7C0-50	2244	2216	2183	2161	2152	2147
CMA 17C0-50	2025	1992	1959	1924	1916	1908
CMP 4C0-50	2408	2399	2390	2387	2384	2382
CMP 10C0-50	2263	2224	2197	2191	2186	2180
CMC 4C0-50	2324	2318	2307	2304	2304	2302
CMC 10C0-50	2103	2072	2047	2039	2036	2034
CMA 7C1-50	2248	2220	2187	2164	2156	2150
CMA 17C1-50	2018	1987	1954	1919	1911	1903
CMC 4C1-50	2318	2309	2301	2295	2295	2295
CMC 10C1-50	2106	2078	2052	2047	2042	2039

Figure 3.9(b) shows the influence of the addition of 1% Portland cement on the Marshall force resisted, measured at different curing times in CMA and CMC materials. It can be observed that cement addition improved the strength of all the materials studied, which is consistent with results found by Fang et al. (2016), where the cement increased the strength of CMA specimens.

By comparing the forces resisted by CMA and CMC in Figure 3.9(b), it was found that CMC with 4% of capsules increased its strength throughout the curing period, while CMC with 10% of Ca-alginate capsules specimens nearly stopped gaining strength after 7 days curing, which may be due to the combination of excess of water, which reduced the strength of the specimens, and an excessive pore size, which limited capillary evaporation from the test specimens (Saadoon et al. 2017). Adding 1% of cement was not enough to fully overcome this problem. Finally, by comparing all the water content results of Table 3.3 with the Marshall forces in Figure 3.9(a) and (b), one can conclude that the strength of all the materials studied is approximately inversely proportional to the amount of water present in the mixture, independent of the binder used.

3.4 Summary

This chapter has been prepared in the frame of research focused on the development of Cold Mix pavement materials made with calcium-alginate capsules (CMC) rather than with just bitumen emulsion, as is normally done. The initial objective was to remove most of the water in cold mix asphalt by encapsulating bitumen droplets. The encapsulation method allowed the preparation of polynuclear capsules with bitumen emulsion encapsulated, with a membrane made of calcium-alginate. Capsules were mixed with aggregates at ambient temperature. During mixing, it was the intention that the capsules containing bitumen emulsion would break, release their content and coat the aggregates. To study CMC, an extensive experimental programme has been carried out to evaluate the effect of compaction energy, cement content, curing time and binder type on the mechanical properties of CMC. It was found that CMC test samples increased their Marshall stability linearly with the increase of the compaction energy. Test samples could be demoulded immediately after compaction. Furthermore, the Marshall stability of CMC increased with curing time, and the general strength improved with increasing amount of capsules in the mixture. It was found that the bitumen in CMC did not play an important role in the strength of the pavement material, as much remained encapsulated, but that strength gains came mainly from the alginate in the capsules. In short, cold mix pavement materials made with calcium-alginate (Ca-alginate) capsules is a novel material for pavements that has shown potential to be an alternative for conventional cold mix asphalt made with bitumen emulsion.

Chapter 4: Cold Mix made with Calcium-alginate Capsules that Contain Bitumen Emulsion and Rapid hardening Cement

4.1 Introduction

Limited studies have examined the use of rapid hardening cements to evaluate the performance of cold mix asphalt (CMA), see Section 2.6.3.

This chapter aims to accelerate the reaction of Cold Mix pavement material made with calcium-alginate capsules (CMC) that contain bitumen emulsion by using rapid hardening cements instead of Portland cement. Therefore, the effect of compaction energy, curing time, rapid hardening cements and Portland cement additions on the mechanical properties of cold mix pavement material made with Ca-alginate that contains bitumen emulsion have been evaluated.

4.2 Materials and Methods

4.2.1 Materials

Materials for capsules consisted of a cationic bitumen emulsion, sodium alginate ($C_6H_7O_6Na$) and calcium chloride ($CaCl_2$), as mentioned previously in Section 3.2.1. The aggregate used was a well-graded crushed limestone, with size between 14mm and a few microns as shown in Figure 4.1(b). Note that the gradation was slightly different from that used in Chapter 3, for more details, see Appendix B. The rapid hardening cements and Portland cement used were calcium sulfoaluminate cement (CSA), provided by Italcementi Ltd, Italy; Ciment Fondu type calcium aluminate cement (CAC), provided by Firetile Ltd, UK; and Portland cement type CEM I 32.5 N, provided by Hanson Cement Ltd, UK.

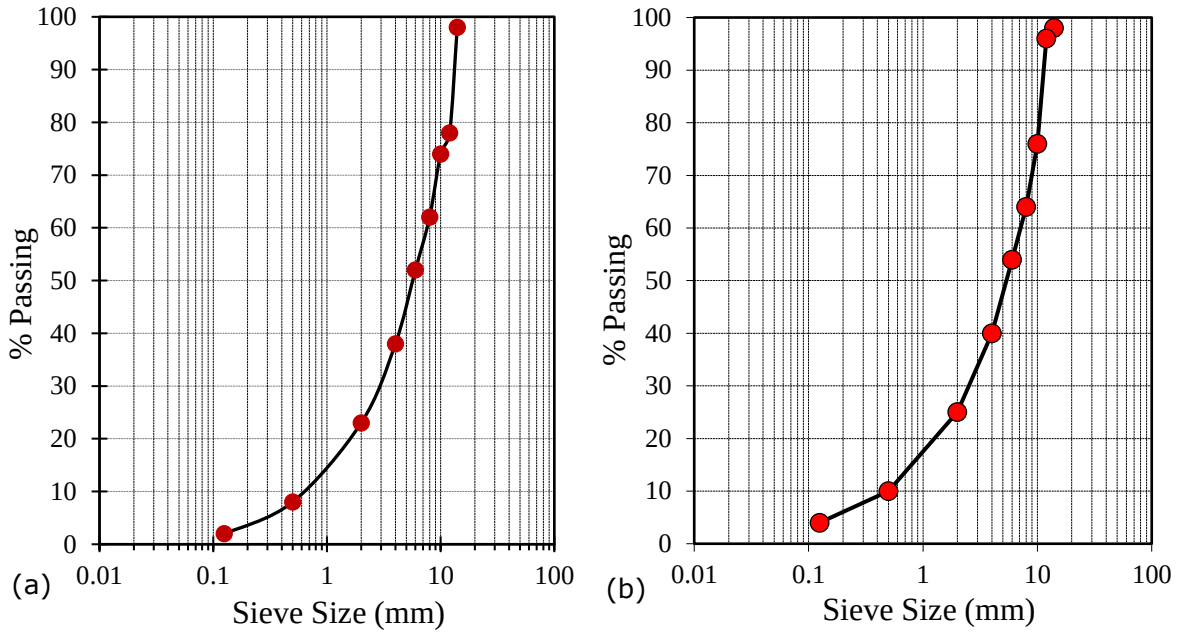

Figure 4.1 Aggregate size distribution used in (a) Chapter 3, and (b) Chapter 4.

4.2.2 Encapsulation Procedure

Ca-alginate capsules containing bitumen emulsion and Ca-alginate particles (with 67% and 73% water content respectively) were fabricated by the same procedure defined in Section 3.2.2 and shown in Figure 3.3(a) and (b).

4.2.3 Test Specimens Preparation

Marshall test specimens, with and without rapid hardening cement addition, were prepared (with 100 mm diameter and 50 mm height); see, as an example, Figure 3.4. The manufacturing process for the 16 different types of mixture evaluated in this study is shown in Table 4.1. Mixes containing 3060 g of aggregates were manufactured in batches with raw materials such as Ca-alginate capsules that contain bitumen emulsion and Ca-alginate particles with, and without, rapid hardening cement addition. The amount of raw materials was added by total weight of aggregates, see Table 4.1. Note that the amount of water in each mixture used for the Marshall test specimens with, and without, rapid hardening cement was 2.5%.

Table 4.1 Composition and manufacturing process used for the mixtures studied.

Mixture type	Manufacturing process description	Abbreviation	Purpose
Cold Mix pavement material made with calcium-alginate Capsules (see Figure 3(a)) that contain bitumen emulsion (CMC)	The manufacturing process for the Marshall test specimens made with 4% Ca-alginate capsules that contain bitumen emulsion, with and without cement, was the same as described in Table 3.1. Additionally, the Marshall test specimens of CMC with rapid hardening cements were also manufactured in this order: first the coarse aggregates, then 4% w/w of calcium-alginate capsules (%Cap: 4) and 1%, 2% or 3% of rapid hardening cement (%Rapid Cem: RA1; RS1, RA2; RS2 and RA3 and RS3, respectively) were mixed for 2 min at 20±1ºC, followed by 60s of mixing by hand. Finally, the mixture was poured into Marshall moulds and compacted by applying 20, 40, 50, 70, 80 or 100 blows (N_{Blows}: 20, 40, 50, 70, 80, 100, respectively) on each flat face of the specimens.	*The Abbreviation for the Marshall test specimens made with 4% Ca-alginate capsules that contain bitumen emulsion, with and without cement, was the same as described in Table 3.1.* CMC %Cap %Rapid cem - N_{Blows} *e.g. CMC 4RAC1-50 or CMC 4RSC1 means that 4% w/w of capsules were used, 1% w/w of rapid aluminate cement or rapid sulfoaluminate cement was added and, 50 blows were applied to compact the mixture.*	The same as described in Table 3.1.
Cold Mix pavement material made with calcium-alginate Particles (see Figure 3(b)) (CMP)	The manufacturing process for the test specimens made with 4% Ca-alginate particles (CMP) was the same as described in Table 3.1.	*The Abbreviation for the Marshall test specimens made with 4% Ca-alginate particles was the same as described in Table 3.1.*	The same as described in Table 3.1.

4.2.4 Marshall Stability Test

The Marshall stability test procedure described in Section 3.2.7, was also carried out, for the average of 3 test specimens with, and without, rapid hardening cements addition in the CMC.

4.2.5 Curing Process of the Test Specimens

All the Marshall test specimens with, and without, rapid cement addition (see Table 4.1) were also cured by the same procedure as described in Section 3.2.8.

4.2.6 Water Content in the Test Specimens at Different Curing Times

Water content in the Marshall test specimens was measured following the procedure described in Section 3.2.9.

4.2.7 Amount of Water Bound by Cement

The amount of water bound by cement in the CMC was quantified by the following procedure:

- First, 72 test specimens for CMP 4C0-50, CMC 4C1-50, CMC 4RA1-50 and CMC 4RS1-50 were prepared, see Table 4.1. Then, all the Marshall specimens within the moulds were placed at room temperature, 20±1ºC, and relative humidity of 60% for 24h. Next, all the Marshall test specimens were demoulded and placed at room temperature in order to quantify the water evaporation by mass loss at different curing times: 1, 3, 7, 14, 21 and 28 days. The water evaporation was quantified by weighing the specimens using a balance, with a precision of 0.5g. The evaporation of water was quantified at room temperature instead of quantifying it by oven because heating at a high temperature of more than 100±1ºC for a long time will induce further hydration of the cement and loss of volatile components (Fang et al., 2016).

- After 28 days, all the Marshall test specimens, were left at room temperature for a further 7 days until mass loss due to evaporation was assumed to have stopped. Then, all the test specimens were crushed into pieces with a maximum of 5 mm in size. These pieces of the Marshall test specimens were dried in an oven at 105ºC, in order to obtain the average trapped water in the mixture used for the Marshall

test specimens of CMP 4C0-50, CMC 4C1-50, CMC 4RA1-50 and CMC 4RS1-50, respectively.

Finally, the amount of water bound by the cement, at different curing times, was quantified using the following procedure: first, based on a study by Fang et al. (2016), the residual evaporable water content in CMC with cement was quantified by Equation (4.1). Second, it was assumed that the residual evaporable water content is zero and the amount of water bound by the cement at different curing times was quantified by Equation (4.2).

$$\boldsymbol{p_{ev,res}(t) = \left(p_{tot} - p_{bou}(t) - p_{trap} - p_{ev}(t)\right)} \quad (4.1)$$

$$\boldsymbol{p_{bou} = \left(p_{tot} - p_{trap} - p_{ev}\right)} \quad (4.2)$$

where P_{tot} is the total percentage of water in the average of 3 test specimens, with or without cement; P_{trap} is the percentage of water trapped in the CMP without cement or CMC with cement; P_{ev} is the percentage of water of evaporation, at time *t*, in the CMP without cement or CMC with cement. Figure 4.2 shows a schematic diagram for the distribution of water in the total CMC with cement addition.

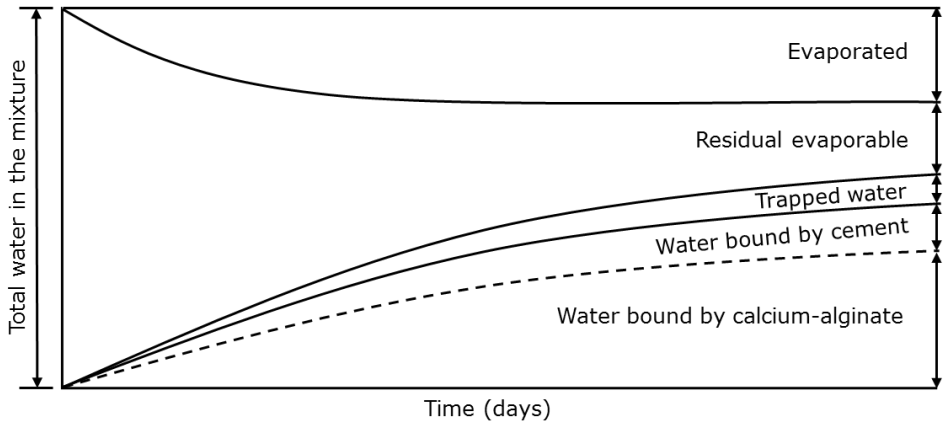

Figure 4.2 Schematic diagram for the distribution of water in the total CMC with cement addition.

4.3 Results and Discussion

4.3.1 Effect of Compaction Energy and Rapid Hardening Cement addition on the Marshall Strength of CMC

Figure 4.3 shows the average Marshall force resisted by CMC test specimens with 3 different cement content additions for both rapid hardening cements and Portland cement, after 24h curing, at 20ºC. From Figure 4.3, it can be observed that the average force resisted by the mixes containing rapid hardening cements was improved over that of the CMC mixes containing Portland cement. It was found that the force resisted by the CMC specimens with calcium aluminate cement was greater than that resisted by the CMC specimens with the same mass of Portland cement, while the force resisted by the CMC specimens with the same mass of calcium sulfoaluminate cement was always substantially higher than both the other cement-treated test specimens with the same dosage (Table 4.2) demonstrating the importance of cement chemistry for mix strength.

Table 4.2 Variation in the Marshall force resested in kN by CMC test specimens, after 24h curing at 20°C due to the effect of Marshall compaction configurations and rapid hardening cement addition as well as Portland cement addition.

Mixture type	Number of blows					
	20	40	50	70	80	100
CMC 4C0	1.50	3.62	4.45	4.77	5.94	6.27
CMC 4C1	2.44	4.03	5.63	7.05	7.97	8.53
CMC 4C2	3.19	5.08	5.85	7.81	9.16	10.13
CMC 4C3	4.48	5.63	6.13	8.32	9.71	11.37
CMC 4RA1	5.41	6.9	7.49	9.45	11.11	12.32
CMC 4RA2	6.13	8.05	9.23	10.54	11.84	13.51
CMC 4RA3	6.75	8.98	10.57	12.31	13.94	14.26
CMC 4RS1	7.79	9.53	11.37	12.97	14.89	15.84
CMC 4RS2	8.93	10.66	12.56	14.36	17.09	18.41
CMC 4RS3	9.92	11.62	13.31	15.84	18.03	19.39

Finally, Figure 4.3 also shows that:

1) The strength of the CMC test specimens increased approximately linearly with the

number of blows applied irrespective of cement and mass, and

2) The force resisted by the CMC mixes increased by increasing the amount of cement for both rapid hardening cements and Portland cement. It is unclear if the evolution of strength was mainly dependent on the hydration properties of the cement or some kind of beneficial interaction between the cement's hydration product and calcium-alginate. Further research is still required to understand the reason for this.

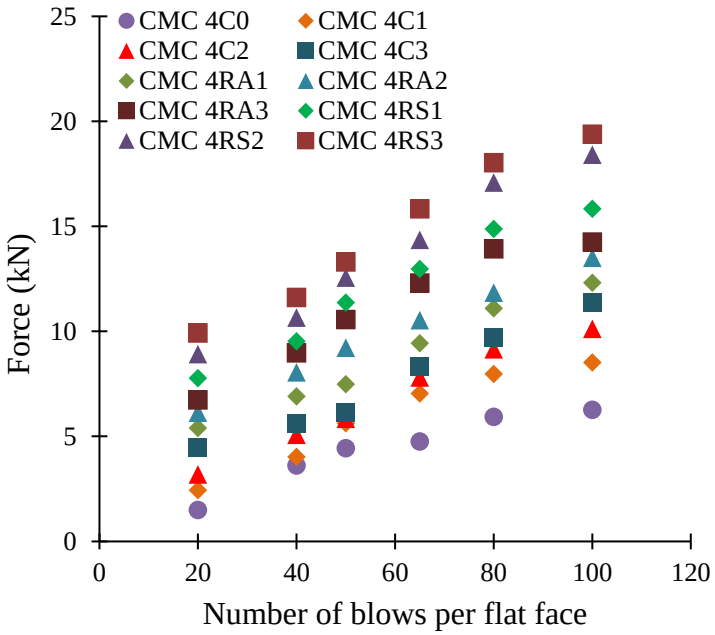

Figure 4.3 Variations in the Marshall force resisted by CMC test specimens, after 24h curing at 20°C due to the effect of Marshall compaction configurations and rapid cement addition as well as Portland cement addition**.**

4.3.2 Influence of Rapid hardening Cements on the Marshall strength of CMC at Different Curing Times

Figure 4.4 shows the average Marshall force resisted at different curing times, for CMP 4C0, CMC 4C0, CMC 4C1, CMC 4RA1 and CMC 4RS1 compacted with 50 blows on each flat face. From Figure 4.4, it can be concluded that:

1) The force resisted for all test specimens increased with curing time, and

2) The strength of CMC materials with 1% of cement depended on the type of cement used, i.e., Portland cement, calcium aluminate cement, calcium sulfoaluminate cement added to the mixture.

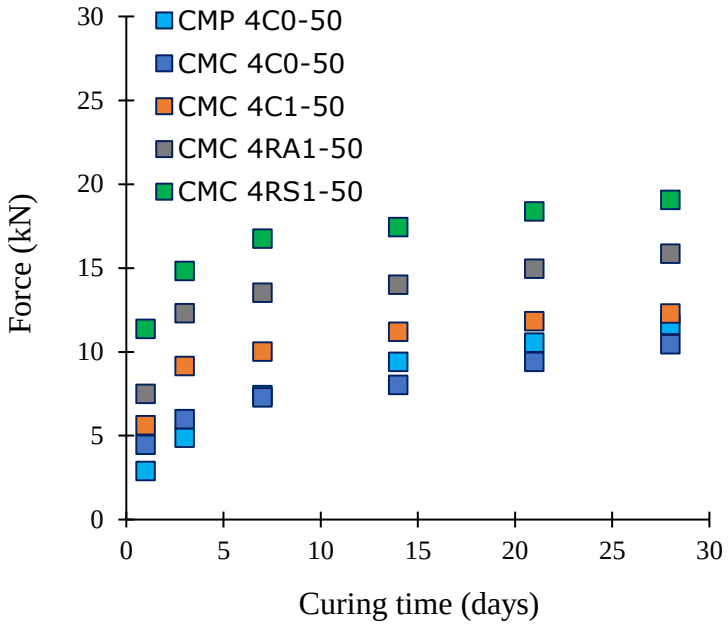

Figure 4.4 Marshall force resisted measured at different curing times for CMC specimens, with and without 1% of cement.

In Figure 4.4 it can be observed that the force resisted by CMC 4RA1-50 and CMC 4RS1-50, after 1 day curing, increased 1.33 times and 2.02 times respectively compared to CMC 4C1. Furthermore, for the CMC 4RA1-50 and CMC 4RS1-50, the force resisted, after 28 days curing, increased 1.29 times and 1.55 times compared to that of the CMC 4C1-50.

Fang et al. (2016) found that, for CMA specimens with Portland, calcium aluminate and calcium sulfoaluminate cement, a part of the water became bound into the hydration products and could not be evaporated, at different curing times. A similar response is seen in Figure 4.5.

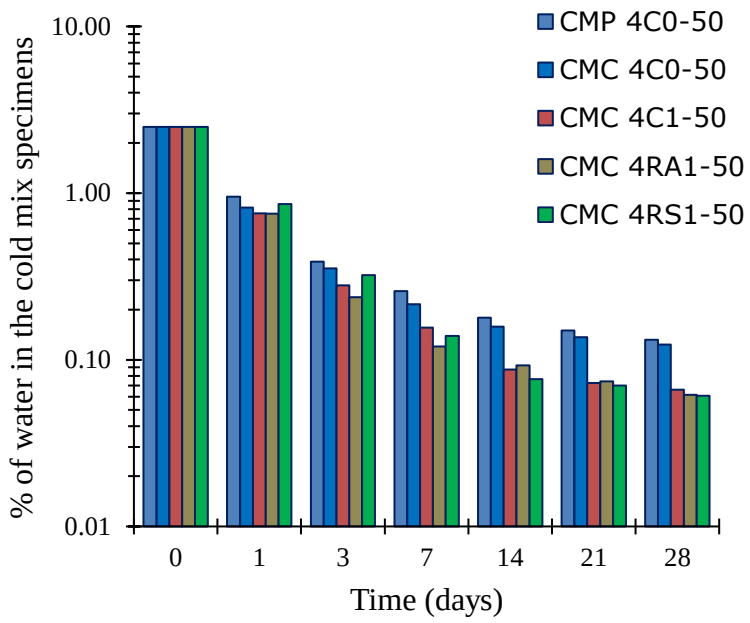

Figure 4.5 Water content measured at different curing times for CMC specimens with and without 1% of cement.

Figure 4.4 compares the influence of the addition of 1% Portland cement and rapid hardening cements on the Marshall forces at different curing times. The strength of CMC 4RS1-50 was always substantially higher than that of CMC 4RA1-50 and CMC 4C1-50 throughout the curing period. This greater strength may be due to the fact that the amount of water bound with calcium sulfoaluminate cement at early age was higher than that bound by the calcium aluminate cement or Portland cement.

4.3.3 Water Binding with Rapid hardening Cements

The amount of water bound with rapid hardening cements in the CMC materials was quantified according to the procedure described in Section 4.2.5. The initial amount of water in each mixture used for the Marshall test specimens with and without cement was 2.5%. The water that had already evaporated at time *t* is shown in Table 4.3, and the trapped water in each mixture used for the Marshall test specimens with CMP 4C0-50, CMC 4C0-50, CMC 4RA1-50 and CMC 4RS1-50 was 0.031%. From Table 4.3, it can be observed that the mass loss due to water evaporation in the CMP 4C0-50 was lower than

that of specimens with cement, the reason for which is unclear in this study but probably due to the interaction between cement hydration product and calcium-alginate helps to increase the mass loss in the test specimens with cement, although further research is still required to understand the reason for this. Neither is it expected for all the test specimens to have the same amount of trapped water. However, this must mean that the surface pore accessibility is the same for all, as evaporation will stop when the suction retains water in opposition to its tendency to evaporate.

Table 4.3 Amount of evaporation water in % w/w of the cold mix specimens measured at different curing time.

Mixture type	Time (days)					
	1	3	7	14	21	28
CMP 4C0-50	1.62	2.09	2.22	2.3	2.37	2.4
CMC 4C1-50	1.73	2.2	2.31	2.35	2.39	2.42
CMC 4RA1-50	1.73	2.24	2.32	2.38	2.4	2.41
CMC 4RS1-50	1.75	2.26	2.34	2.4	2.41	2.42

Figure 4.6 shows the amount of water bound vs curing time, with 1% of rapid hardening cements and Portland cement in the CMC materials, quantified according to Equations 4.1 and 4.2. This result in Figure 4.6 shows that the bound water content increases with curing time for all mixes and that the amount of water bound by the rapid hardening cements increased more than with the Portland cement. These results help to explain why the Marshall strength in the test specimens (see Figure 4.4) increased with rapid hardening cements more than with the Portland cement, at different curing time. Furthermore, in Figure 4.6, it can be seen that the amount of water bound due to hydration by the CMC 4RS1-50 increased more than that of other test specimens throughout the curing period, which helped to explain why the Marshall strength in the CMC 4RS1 (see Figure 4.4) increased more than did the other test specimens throughout the curing period.

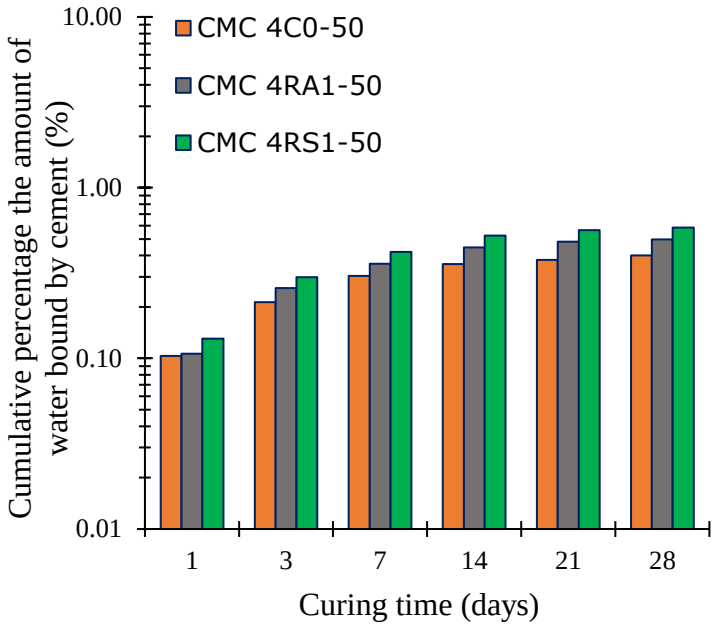

Figure 4.6 Amount of water bound measured at different curing time for CMC 4C1-50, CMC 4RA1-50 and CMC 4RS1-50.

4.3.4 Hardening Process

Figure 4.7(a) and (b) shows a schematic representation of the hardening process for CMP without cement, and CMC with cement, which is divided into 4 stages. Cold mix pavement material made with calcium-alginate (CMP) was evaluated with respect to Chowdary et al. (2009) who believed that this calcium-alginate polymer can form a viscous microenvironment upon hydration.

In Stage 1, shown in Figure 4.7(a) and (b), it can be seen that the test specimens made with CMP without cement and CMC with cement are wetted by the calcium alginate particles and calcium alginate capsules that contain bitumen emulsion respectively. Some of the capsules are so strong that they do not break during compaction, see Figure 4.7(b). This happens because the capsules may need more compaction energy. If they break, the released emulsion might help the bonding of the aggregates and therefore increase the mechanical strength of the mixtures.

In Stage 2, shown in Figure 4.7(a) and (b) the cold mix specimens start hydrating and drying once they are exposed to room temperature, 20 ± 1^{0}C and relative humidity of 60%.

The evaporation rate depends on the ambient temperature, relative humidity, the air voids content of the mixtures and the competition between the drying and the binding of water into cement-hydration products (Scherer, 1990; Lura et al., 2007; Lehmann, 2009). Based on the results of this study, there is an extremely clear relationship between the drying and the binding of water into hydration products of cement and calcium-alginate in CMC materials, at all curing times, see Table 4.3 and Figure 4.6.

In Stage 3, shown in Figure 4.7(a) and (b), during the drying process, the evaporation rate increases in the specimens with cement more than in the test specimens without cement (see Table 4.3), and the cement acts as binder, and the mechanical strength increases with time (see Figure 4.4). Based on the test results, adding 1% of Portland cement in CMC materials helped to increase the strength at different curing times, while adding 1% of rapid hardening cement in the CMC materials further increases this benefit for the same treatment level. This is because the rapid hardening cement in the CMC materials binds a higher amount of water than Portland cement at all curing times, see Figure 4.6.

Finally, in Stage 4, shown in Figure 4.7(a) and (b), the amount of free water for CMP without cement and CMC with cement respectively reduces until it has practically all evaporated. The low amount of bitumen emulsion in capsules reverts to bitumen, while the hydrated products of Ca-alginate and cement, act as a binder and both bind the aggregates. The reaction between cement and Ca-alginate may possibly produce other hydration products. Further research is required to study the interaction of the cement's hydration products with the Ca-alginate capsules' materials.

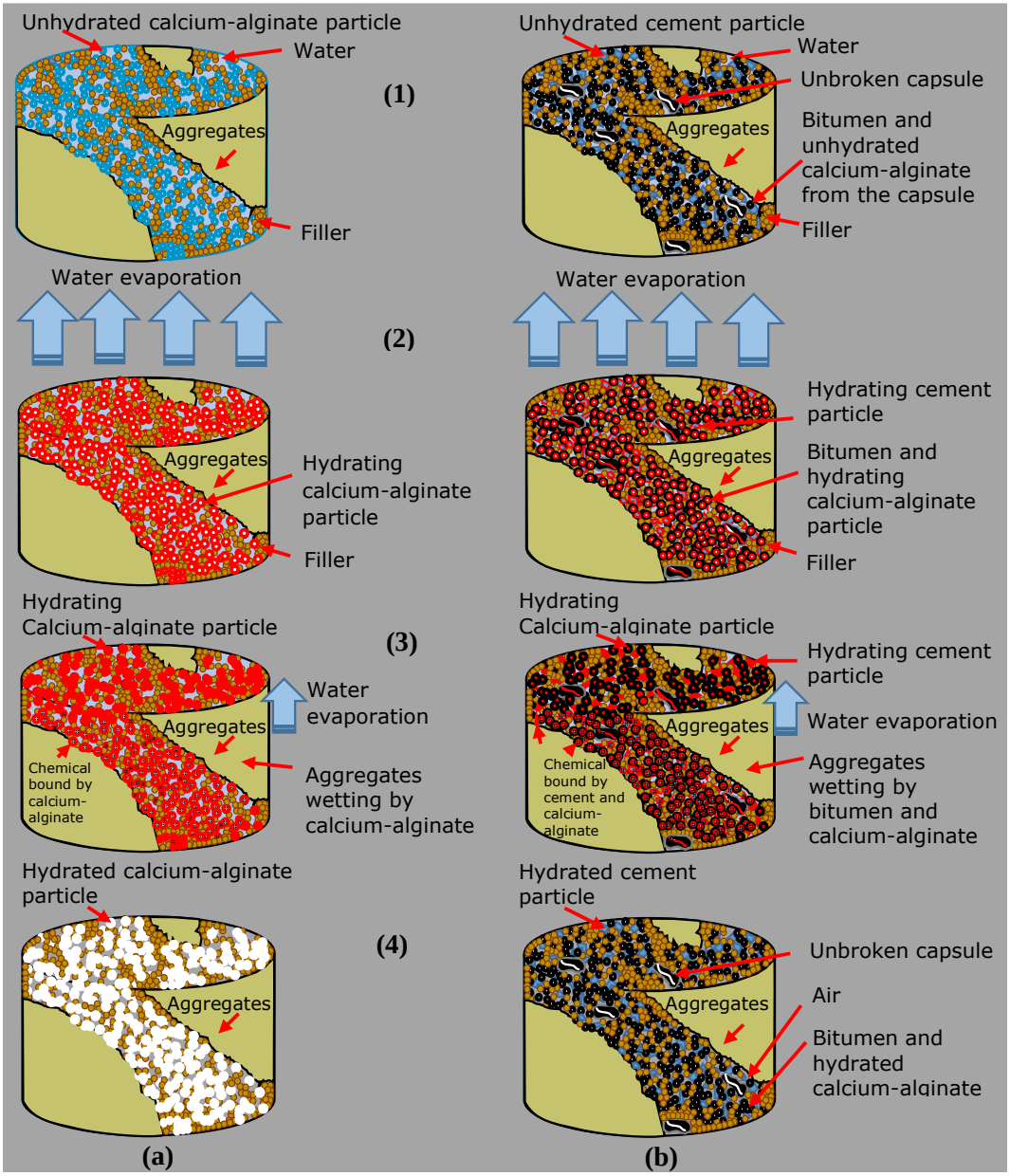

Figure 4.7 Schematic representation of the hydration process for (a) CMP without cement (b) CMC with cement.

4.4 Summary

This chapter has been prepared to accelerate the reaction of Cold Mix pavement material made with calcium-alginate capsules (CMC) that contain bitumen emulsion by using rapid hardening cement instead of Portland cement. The encapsulation method was the same as defined in Section 3.2.2. The components of the Marshall test specimens (capsules or particles, aggregates and cement) were mixed and then compacted at ambient

temperature. An experimental programme was carried out to evaluate the effect of compaction energy, curing time, rapid hardening cement and Portland cement additions on the mechanical properties of cold mix pavement material made with capsules or particles. It was found that CMC test specimens with rapid hardening cements improved their Marshall stability approximately linearly with increase of the compaction energy compared to the stability values achieved by the addition of Portland cement. Furthermore, the Marshall stability of test specimens made with rapid hardening cements, was always higher than that of test specimens made using Portland cement in the CMC materials at each curing time. It was found that the greater strength in the CMC materials with rapid hardening cements correlated with the amount of water bound and the rate of evaporation at different curing times. In short, the rapid hardening cements have shown the potential to be an alternative for Portland cement in the cold mix pavement materials made with calcium-alginate capsules that contain bitumen emulsion.

Chapter 5: Moisture Resistance of Cold Mix made with cement-treated Calcium-alginate Capsules that Contain Bitumen Emulsion

5.1 Introduction

Many studies have applied different curing protocols (Jenkins, 2000; Bocci et al., 2002; Thanaya, 2003; Serfass et al., 2004; Oke, 2011) and moisture damage protocols (James et al., 1996; Brown and Needham, 2000; Oruc et al., 2007; Al-Busaltan et al., 2012; Al-Hdabi et al., 2013; Al-Hdabi et al., 2014) in order to measure the mechanical performance of conventional cold mix asphalt (CMA) at different curing times, see Section 2.5.1 and 2.5.2. Existing literature (Terrell and Wang, 1971; Schmidt et al., 1973; Head, 1974; Li et al., 1998; Thanaya, 2003; Oruc et al., 2007; Garcia et al., 2013; Fang et al., 2013), see Section 2.6.2 and 2.6.3 describes the effect of curing protocols on the mechanical properties for CMA with and without cement. Furthermore, Section 2.6.5 describes the effect of moisture damage protocols on the mechanical properties for CMA with and without cement.

This chapter aims to evaluate the mechanical performance, at dry and wet condition, for CMC materials, with and without cement.

5.2 Materials and Methods

5.2.1 Materials

The aggregates, bitumen emulsion and the raw materials for Ca-alginate capsules were the same as described in Section 3.2.1. Additionally, calcium sulfoaluminate cement as described in Section 4.2.1, was used to improve the moisture damage in CMC materials.

5.2.2 Encapsulation Procedure

The proportions of materials and encapsulation procedure for Ca-alginate capsules that contain bitumen emulsion were the same as defined in Section 3.2.2.

5.2.3 Test Specimen Preparation

Marshall test specimens for CMA, CMC with and without cement, were prepared (with 100 mm diameter and 50 mm height), see as an example Figure 3.4. All Marshall test specimens have been compacted with 50 blows on each flat face. The amount of aggregates and the manufacturing process for the 4 different types of mixtures evaluated in this study are described in Section 3.2.3 and 4.2.4.

5.2.4 Curing and Moisture Damage Protocol of Test specimen's

The curing and the moisture damage protocol used for the test specimens, with and without cement, was divided into two groups as follows:

- Dry condition: After compaction, the test specimens within the moulds for CMA 7C0-50, CMC 4C0-50 and CMC 4RS1-50, were placed at room temperature of 20±1ºC and relative humidity 60% for 24 h. Then, all the test specimens were demoulded and cured for 7 and 28 days at room temperature. This curing period was fixed to ensure uniform treatment for all the test specimens.

- Wet condition: After the same demoulding and curing the test specimens were subjected to a vacuum with 6.7 kPa pressure for 30±5 minutes, and then immersed in a water bath for 3 days at 40°C, as recommended by EN 12697-12. Finally, all test specimens were divided into two groups: the first group was soaked for 2h at 20°C and the second group was tested immediately (i.e. at 40°C). Hence specimen ages were 10 and 31 days old in total.

When cement is in use, it has rapid hardening properties, so almost all strength and stiffness gain is expected to have been completed in the first 7 days such that testing at

10 day age is not expected to give materially different results than at 7 days. The difference in properties due to an age of 31 days rather than 28 days will be even less significant. When cement is not in use, a comparison of 7 and 10 day-old results may be influenced a little by age, and this effect will be evaluated separately.

5.2.5 Laboratory Testing Program

The laboratory testing program developed for the asphalt mixture specimens was divided into four different groups (see Table 5.1):

- Group 1: Marshall stability tests (MST) were selected as a measure of the compressive strength of the materials, with the average of 3 test specimens being recorded, with and without cement, at dry and wet conditions.

- Group 2: Indirect tensile stiffness modulus (ITSM) tests, were used for the average of 3 test specimens, with and without cement, at dry and wet condition.

- Group 3: Indirect tensile strength (ITS), was applied for the average of 3 test specimens, with and without cement, at dry and wet conditions.

- Group 4: The Repeated load axial test (RLAT) was selected to evaluate the resistance to permanent deformation for the average of 3 test specimens, with and without cement, at dry and wet conditions.

Table 5.1 Experimental programme test for CMA specimens, with and without cement.

Test	Standards	Dry condition	Wet condition
Mechanical properties for Group 1, 2 and 3			
MST @ 20°C ITSM @ 20°C ITS @ 20°C	EN 12697-34 EN 12697-26 EN 12697-23	Curing at 20°C for 7 or 28 days.	Curing at 20°C for 7 or 28 days + vacuum saturation for 30min + water bath for 3 days at 40°C + 2h at 20°C.
Mechanical properties for Group 4			
RLAT @ 40°C	EN 12697-25	Curing at 20°C for 28 days.	Curing at 20°C for 28 days + vacuum saturation for 30min + soaking in water bath for 3 days at 40°C.

5.3 Results and Discussion

5.3.1 Marshall Stability Test (Group 1)

Figure 5.1 shows the Marshall force resisted, at 20ºC, in the dry and wet condition, after 7/10 and 28/31 days curing, for CMA and CMC test specimens, with and without cement. Results and discussion related to dry condition are given in Section 3.3.3 and 4.3.2. All results show a similar gain in stability value from 7/10 to 28/31 days, this gain being proportionately greatest for the alginate capsule-treated mixes (approximately 40% increase) and proportionately least for the sulfoaluminate cement and capsule mixes (even though, overall, these are strongest).

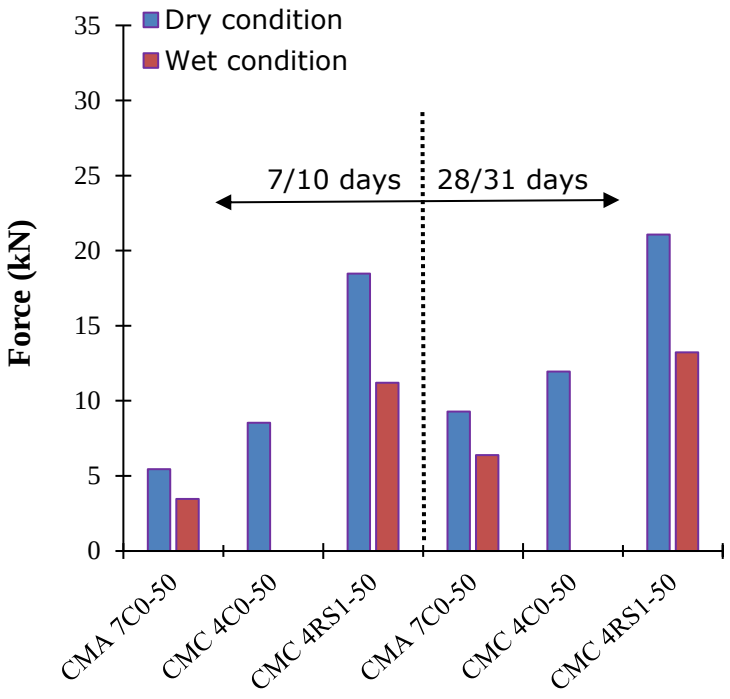

Figure 5.1 Marshall force resisted measured, at dry and wet conditions, after 7/10 and 28/31 days curing time for the CMA and CMC, with and without cement.

Figure 5.1 shows that the force resisted, under wet conditions, for the CMA 7C0-50 specimens after 7/10 and 28/31 days of curing was 36% and 31% respectively lower than the force resisted by specimens in the dry conditions, while the CMC 4C0-50 test specimens, at wet condition, after 7/10 and 28/31 days curing, collapsed after being

exposed to vacuum. This collapse may have been due to insufficient bitumen emulsion or calcium-alginate in the CMC material.

Figure 5.1 shows that the force resisted by CMC 4RS1-50 specimens, at wet condition, after 7/10 and 28/31 curing was 39% and 37% respectively lower than the force resisted by specimens in the dry conditions. This is a similar reduction due to moisture as experienced by the CMA specimens, but the much higher initial (dry) strength achieved by use of capsules improved with 1% of sulfoaluminate cement more than compensates for the deterioration of performance due to wet curing.

5.3.2 Indirect Tensile Stiffness Modulus Test (Group 2) and Indirect Tensile Strength Test (Group 3)

Figure 5.2 (a) and (b) shows the stiffness modulus and indirect tensile strength measured, at 20ºC, in the dry and wet condition, after 7/10 and 28/31 days curing, for CMA and CMC test specimens, with and without cement.

- **Dry condition**

The results in Figure 5.2 show that the CMA and CMC test specimens, with and without rapid hardening cement, gained stiffness modulus and tensile strength, between 7/10 days curing time and 28/31 days of curing time. The results for the emulsion (CMA) mixes are consistent with the literature (Needham, 1996; Brown and Needham, 2000; Miljkovic, 2014; Ojum, 2015; Nassar, 2016). The results also confirm that the stiffness modulus and tensile strength in emulsion mixes can be improved by adding cement (Needham, 1996; Brown and Needham, 2000; Ojum, 2015; Nassar, 2016). The stiffness modulus and tensile strength (see the CMC results) with CMC 4C0-50 specimens were greater than the CMA 7C0-50 specimens, see Figure 5.2. Additionally, the stiffness modulus and tensile strength of CMC 4RS1-50 specimens were greater than for the other cement treated mixes (see Section 4.3.2). This is because the addition of CSA in the CMC material always binds more water than CAC and OPC, see Figure 4.6.

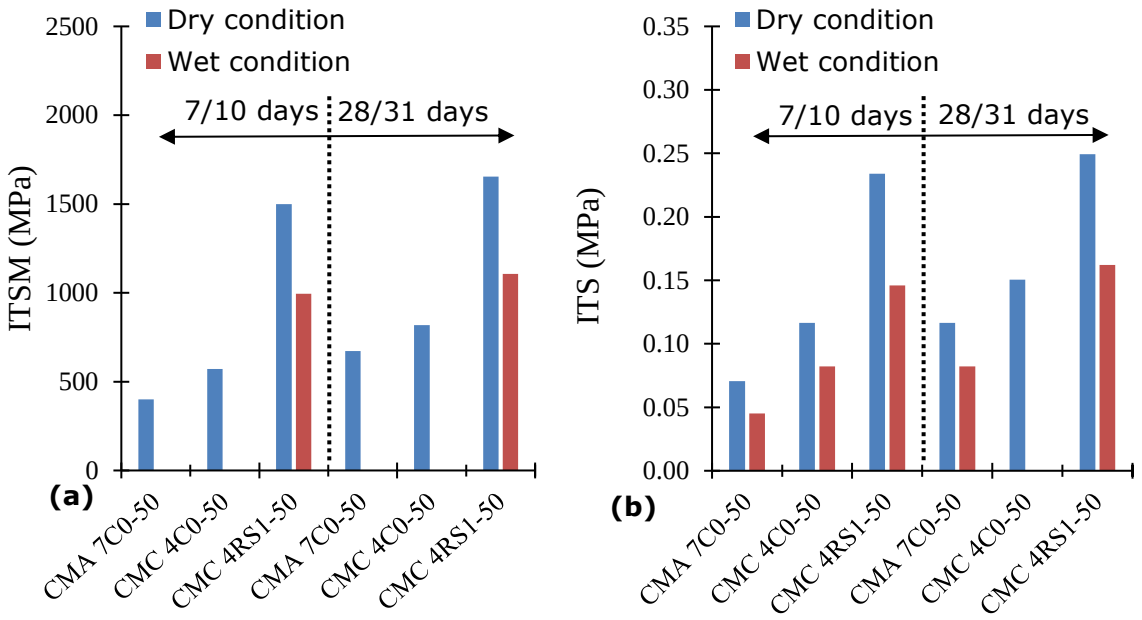

Figure 5.2 (a) stiffness modulus and (b) indirect tensile strength measured, at dry and wet conditions, after 7/10 and 28/31 days curing time for the CMA and CMC, with and without cement.

- **Wet condition**

The response after wet curing is similar to the results reported by Oruc et al. (2007), which shows low stiffness of bitumen emulsion at low curing time. However, the stiffness of these emulsion mixes was improved by the addition of cement (Oruc et al., 2007). Furthermore, the results in Figure 5.2(b) show that the tensile strength for the emulsion mixes are consistent with the literature (Gonzalez, 2009; Nassar et al., 2016). Previous studies also show that the tensile strength for the emulsion mixes can be improved by adding cement (Gonzalez, 2009; Nassar et al., 2016). In the case of the calcium-alginate capsule mixes that contain bitumen emulsion, the stiffness modulus and tensile strength for the CMC 4C0-50 test specimens, after 7/10 and 28/31 days curing, collapsed after being exposed to vacuum as mentioned in Section 5.3.1, but it can be improved by adding 1% of sulfoaluminate cement, see Figure 5.2.

5.3.3 Repeated Load Axial Test (Group 4)

Figure 5.3 shows the resistance to permanent deformation measured, at 40ºC, in the dry and wet condition, after 28/31 days curing, for CMA and CMC test specimens, with and without cement. From Figure 5.3, it can be observed that the resistance to permanent deformation for the CMA 7C0-50, at dry condition, is consistent with the literature (Nassar et al., 2016). Additionally, previous studies show that the resistance to permanent deformation for the emulsion mixes can be improved by adding cement (Nassar et al., 2016).

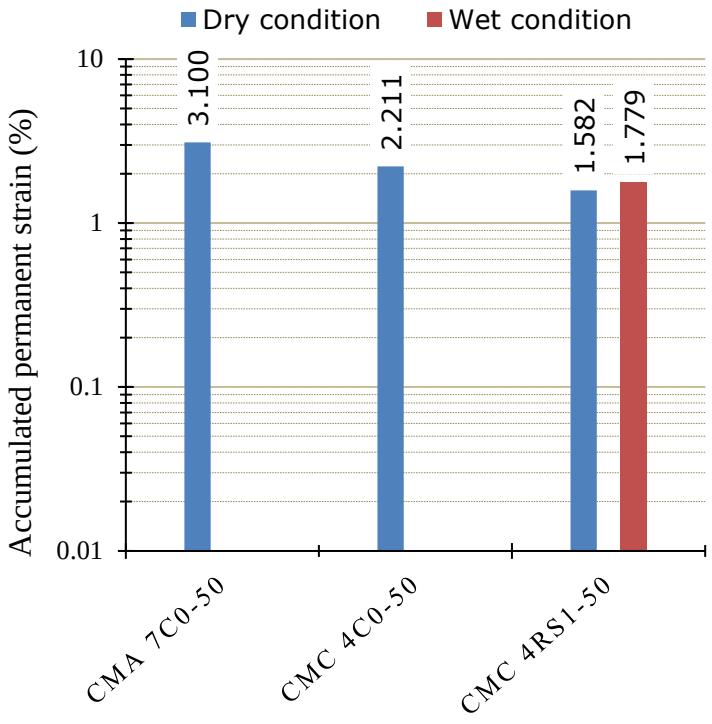

Figure 5.3 Permanent deformation resisted, at dry and wet conditions, after 28 days curing time for the CMA and CMC, with and without cement, compared to the HMA specimens, after 24 hours.

Figure 5.3 shows that the resistance to permanent deformation, at dry condition, for the CMC 4C0-50 test specimens was better than for the CMA 7C0-50 test specimens. At wet condition, the CMA 7C0-50 specimens were completely damaged under the test loading of 100kPa. Likewise, the CMC 4C0-50 test specimens, cured at wet condition collapsed after

being exposed to vacuum as mentioned in Section 5.3.1. The remaining CMC 4RS1-50 materials showed little difference between dry and wet curing results. It seems evident, therefore that wet curing has only a small influence on essentially-compression behaviour but, from the results in earlier sections, has a much greater influence on tensile response. By adding 1% of calcium sulfoaluminate cement to capsule mixes, the resistance to permanent deformation for the CMC 4RS1-50 test specimens was improved, at both dry and wet conditions, see Figure 5.3.

5.4 Summary

This chapter presents a comparison of dry curing and dry curing followed by wet conditioning of the test specimens (soaking them in water) on the mechanical properties of cold mix pavement material made with calcium-alginate capsules (CMC) that contain bitumen emulsion. It was found that CMC specimens were more degraded than the other test specimens when soaked in water after 7/10 and 28/31 days of curing time. When, 1% of calcium sulfoaluminate cement was added to the Ca-alginate capsules the moisture damage of cold mix asphalt reduced after 7/10 and 28/31 days of curing time.

Chapter 6: Overall Discussions

6.1 Review

This chapter will highlight the main findings from this research. It is evident that the force resisted for the cold mix pavement material made with calcium-alginate capsules (CMC) that contain bitumen emulsion increased linearly with the number of blows applied (refer to Chapter 3 and 4). The capsule mixes also confirm that the force resisted can be increased proportionally with the amount of cement addition (refer to Chapter 3 and 4). This chapter will also explore whether the capsule mixes can deliver the same strength as HMA, just by adding 2% of Cement (refer to Chapter 3).

It is further evident from the findings that the force resisted by the CMC, with and without cement addition, increased with curing time (refer to Chapter 3 and 4). The increase of the strength with time is mainly due to the Ca-alginate contained in the bitumen emulsion capsules, which acts as a binder for the aggregates and can produce similar strength without bitumen emulsion (refer to Chapter 3 and 4). Thus, it appears that the alginate is able to polymerize (or increase its degree of polymerization), in the way described in Section 2.11, after mixing with aggregate. It is not known whether there is a minimum proportion of alginate that is required for this polymerization to take place in an aggregate mix, but, if so, it is evident that this is less than 4% by mass.

6.2 Comparison with HMA

Although the amount of bitumen used in the production of the capsules for this study is less than the bitumen for a HMA, CMC with 1% of calcium sulfoaluminate cement, at dry condition, had a strength higher than that HMA, after 7/10 and 28/31 days curing, see Figure 6.1. This sulfoaluminate cement is more effective than other types of cement (refer to Chapter 4).

The average strength was measured for HMA, in a wet condition, and is shown in Figure

6.1. For the same wet condition, after 24 hours curing at 20ºC, the force resisted for the HMA specimens was 13% lower after wet condition curing than the force resisted by specimens cured in the dry conditions. Comparing the Marshall force resisted by the HMA and CMC 4RS1-50, both in wet condition, as shown in Figure 6.1, it was found that CMC 4RS1-50 test specimens, after 7/10 days curing were not that much different in strength, and can be higher than HMA after 28/31 days curing. Further research is required to measure the optimum amount of Ca-alginate capsules and cement for the CMC mix performance, at early life times.

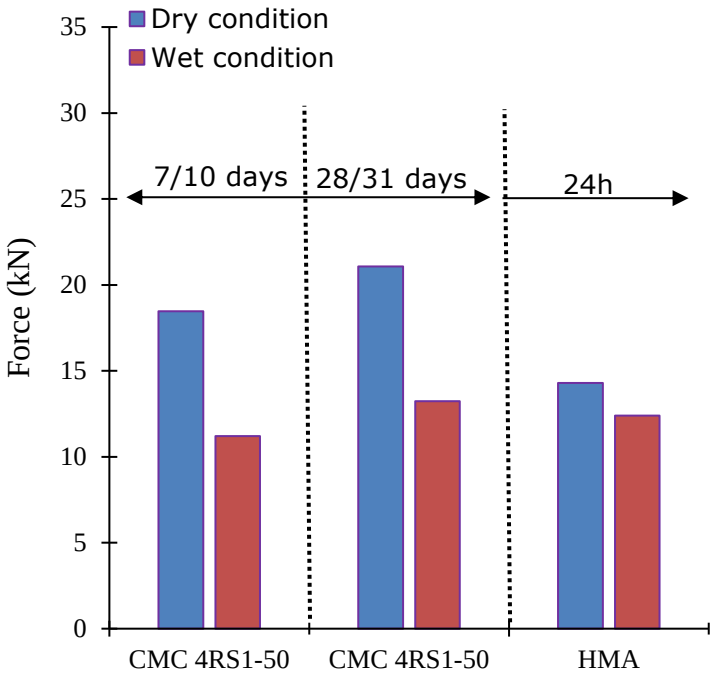

Figure 6.1 Marshall force resisted measured, at dry and wet conditions, after 7/10 and 28/31 days curing time for the CMC 4RS1-50, compared to the HMA specimens, after 24 hours.

Moreover, the greater stiffness and indirect tensile strength, at dry condition, of the calcium sulfoaluminate cement-treated mixes than those of the comparable HMA is evident, as can be seen in Figure 6.2. Furthermore, for the same wet conditions, the indirect tensile strength and stiffness in the CMC 4RS1-50 test specimens, after 28/31 days curing, were higher than those of the HMA.

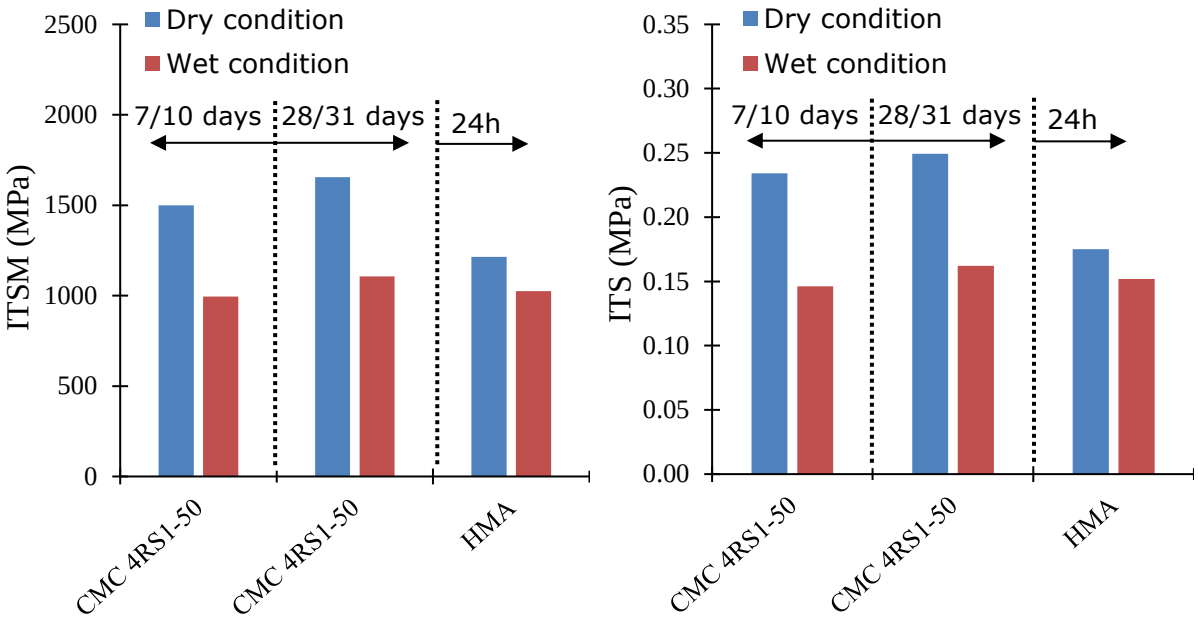

Figure 6.2 (a) stiffness modulus and (b) indirect tensile strength measured, at dry and wet conditions, after 7/10 and 28/31 days curing time for the CMC 4RS1-50, compared to the HMA specimens, after 24 hours.

By comparing the stiffness modulus and indirect tensile strength of the CMC 4RS1-50 and HMA in Table 6.1, it was found that CMC 4RS1-50 test specimens, after 7/10 days curing, had almost the same properties as the HMA. Therefore, from Figure 6.1, a Marshall strength of around 11.2kN at 20ºC for the wet-cured specimens, based on the comparable ITSM and ITS results as for HMA, can be regarded giving a material equivalent to HMA. This simple comparison would, of course need further research to study its validity at high and low temperatures such as 60ºC and -20ºC.

Table 6.1 Average (a) stiffness modulus and (b) indirect tensile strength measured, at wet conditions, after 7/10 days curing time for the CMA and CMC, with and without cement, compared to the HMA specimens after 24 hours.

Test	Mixture type			
	CMA 7C0-50	CMC 4C0-50	CMC 4RS1-50	HMA
	after 7/10 days curing			
ITS (MPa)	0.05	-	0.15	0.15
ITSM (MPa)	-	-	995	1025

Finally, by adding 1% of calcium sulfoaluminate cement to capsule mixes, the permanent deformation for the CMC 4RS1-50 test specimens was slightly reduced relative to the HMA, at both dry and wet conditions, see Figure 6.3. This indicates that the resistance to permanent deformation for the bitumen emulsion capsule mixes plus 1% of calcium sulfoaluminate cement can be greater than that of the reference material, after 28/31 days of curing time even when wet cured.

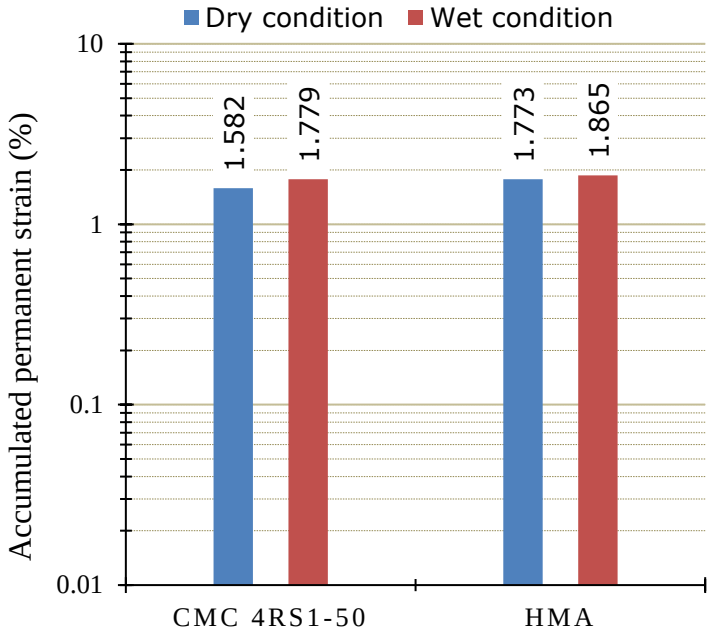

Figure 6.3 Permanent deformation, at dry and wet conditions, after 28/31 days curing time for the CMC 4RS1-50, compared to the HMA specimens, after 24 hours.

6.3 Calcium Alginate as a Potential Binder

As outlined in this research study, alginate has a number of advantages. The alginate is a renewable, natural polysaccharide component and has unique properties, such as non-toxicity and biocompatibility as described in Section 2.10 and 2.12. Alginate can also form particles by using ionic cross-linkers such as calcium-chloride (see example Figure 3.3(b)). Thus, it appears that the Ca-alginate is a potential binder after mixing and compacting with aggregates at ambient temperature 20ºC. It is also evident that the Ca-alginate mixes have good mechanical strength, see Section 3.3.3 and 4.3.2. Moreover, by comparing the Marshall strength of the Ca-alginate mixes, with and without bitumen emulsion, it was

found that:

- The Ca-alginate mixes had similar mechanical strength to Ca-alginate mixes that contain bitumen emulsion, at all curing times (see Section 3.3.3).
- The Ca-alginate mixes had higher mechanical strength than the bitumen emulsion mixes, at all curing times (see Section 3.3.3).
- The moisture damage for Ca-alginate mixes can be improved by adding 1% of calcium sulfoaluminate cement (refer to Chapter 5).
- The moisture damage for Ca-alginate mixes with 1% of calcium sulfoaluminate cement can be less than than that of the HMA (see Section 6.1 and 6.2).

Therefore, when compared to a cold-mix emulsion, it has many practical advantages. However, it was found that the total price to make a Ca-alginate mix with 1% of calcium sulfoaluminate cement, is about 50% greater than the price of bitumen emulsion mixes with 1% of Portland cement, see Table 6.2. But the price would be the same as bitumen emulsion mixes if the total percentage of Ca-alginate is about 2% and this should be a matter for future investigation to see if workable mixes can be made at a reduced alginate dosage. Even at the dosage rates used in this study the increased cost might be acceptable to uses interested in demonstrating a reduction in their global carbon footprint.

Table 6.2 Economic comparison **(**www.alibaba.com and www.sandandgraveldirect.co.uk**)**

Materials	Bulk prices per ton in US$	
7% bitumen emulsion	300	-
4% Ca-alginate	-	1000
1% Portland cement	50	-
1% calcium sulfoaluminate cement	-	200
Aggregates	20	20
Total (100%)	39.9	61

Chapter 7: Conclusions and Recommendations

7.1 Conclusions

In this thesis, investigation into the performance of a new cold mix asphalt type made with bitumen emulsion capsules was performed. Although not the aim at commencement of the study, it is evident that Ca-alginate has binding properties that can replicate and maybe exceed those of bituminous binders.

7.1.1 Conclusions Related to Cold Mix Pavement Material made with Calcium-alginate and Aggregates

Bitumen emulsion, Ca-alginate capsules that contain bitumen emulsion, and Ca-alginate particles were studied with and without adding 1%, 2% and 3% w/w of Portland cement. The mechanical strength of Cold Mix pavement materials made with these binders, was evaluated using Marshall test specimens. The main conclusions were as follows:

- It is practical to prepare Ca-alginate capsules that contain bitumen emulsion and Ca-alginate particles without bitumen, sized between 0.4 mm and 0.74 mm, which can be added inside cold mixes to bind the aggregates during the pavement material's manufacturing process.

- Cold mix specimens made with 4% of Ca-alginate capsules (with and without cement additions) increased their Marshall stability linearly with the increase in compactive effort.

- CT-Scan images of cement treated cold mix specimens containing 4% of Ca-alginate capsules revealed that the bitumen in the capsules did not mix properly in the material. The bitumen added in the capsules played an important role to gain strength only in the first 14 curing days. Ca-alginate was the main binder type that held the aggregates together.

- The Marshall stability of cold mixes increased with the curing time, and this happened due to the evaporation of water from the pavement material.

- Alginate formed an intimate composite with the hydration products of cement, which proved to be very dense and to work well as a binder.

- Cold Mixed pavement materials made with 4% Ca-alginate particles and 2% cement, cured for 7 days can be an alternative to conventional cold mixes made with bitumen emulsion, since they produced a material with equivalent stiffness and strength to Hot Mix Asphalt.

7.1.2 Conclusions Related to Cold Mix made with Calcium-alginate Capsules that Contain Bitumen Emulsion and Rapid hardening Cement

Cold mix specimens made with 4% of Ca-alginate capsules that contain bitumen emulsion and rapid hardening cement (both calcium aluminate and calcium sulfoaluminate) additions were evaluated using Marshall test specimens. It is further concluded that

- Increased their Marshall stability linearly with the increase in compactive effort.

- Increased their Marshall stability with the increase of curing time. This happened due to the evaporation of water from the pavement material.

When 1% calcium sulfoaluminate cement was added, this:

- Was more effective with cold mix specimens made with 4% of Ca-alginate capsules that contain bitumen emulsion than with addition of 1% calcium aluminate cement or 1% Portland cement in regard at a given curing time. This is due to 1% calcium sulfoaluminate cement in the cold mix specimens made with 4% of Ca-alginate capsules that contain bitumen emulsion binding more water than 1% calcium aluminate cement and 1% Portland cement.

- Can be a more effective additive to cold mixes than cold mixes made with calcium aluminate cement or Portland cement, since it produced a material with higher Marshall stability than other cold mixes, after 24h curing.

7.1.3 Conclusions Related to Moisture Resistance of Cold Mix made with cement-treated Calcium-alginate Capsules that Contain Bitumen Emulsion

Cold Mix pavement materials made with: a) 4% Ca-alginate capsules that contain bitumen emulsion, b) 4% Ca-alginate capsules that contain bitumen emulsion with rapid-hardening cement and c) 7% bitumen emulsion were evaluated both dry and wet conditions. It is concluded that:

- The mechanical properties, at dry condition, increased after 7 and 28 days of curing time.

- Materials made with 4% Ca-alginate capsules that contain bitumen emulsion, at 7 and 28 days of curing time, collapsed after being subjected to a vacuum for approximately 30 minutes. The reason for this collapse is not clear but it may be due to not having enough bitumen or calcium-alginate in the mixtures.

- In a wet condition, the mechanical properties after 7/10 and 28/31 days of curing time of cold mix pavement materials made with Ca-alginate capsules that contain bitumen emulsion can be improved by adding 1% of sulfoaluminate cement.

7.1.4 Conclusions Related to overall discussion

The mechanical properties of CMC specimens with 1% of sulfoaluminate cement was compared with those of conventional hot mix asphalt. It is concluded that:

- The mechanical properties of CMC with 1% sulfoaluminate cement (in the presence of water) after 7 days of curing, can be as good as hot mix asphalt. CMC with 1% of calcium sulfoaluminate cement presented higher mechanical performance than hot mix asphalt after 7 and 28 days of curing time.

- The mechanical properties after 28 days of curing time, at wet condition, of CMC with 1% of sulfoaluminate cement, can have higher mechanical properties than the comparable hot mix asphalt.

7.2 Recommendations

This research revealed that CMC material without cement additives cannot achieve the same or higher mechanical performance than that of HMA. Furthermore, based on the analysis of the results of this research, the main recommendations are given as follows.

- Further research is still required to understand the hydration properties of the cement and the interaction of the cement's hydration products in the presence of Ca-alginate.
- The present study in Chapter 3 showed that the mechanical strength of cold mixes at different curing times, did not increase when increasing the amount of binder type, probably as a result of the increase in the water content of the test specimens, although further research is required to confirm this hypothesis.
- Research may also be conducted to measure the optimum amount of Ca-alginate capsules required for adequate mix performance.
- It was observed that the mass loss due to water evaporation in the CMP material was lower than that of the CMC with cement. So, it is recommended that further research be carried out to evaluate the interaction of the cement's hydration products with the Ca-alginate capsule materials at different curing times. For instance the evaluation could be done after mixing the CMC materials with cement by using ESEM.
- It is highly recommended that further research should be done on the use of different contents of calcium-alginate and bitumen emulsion in the production of bitumen emulsion capsules. The aim would be to improve the mechanical performance, in a wet condition curing, of the CMC material.

- Additional study is needed of the combined impact of different levels of humidity and curing temperatures together on the mechanical properties of CMC material, with and without cement. Also, it would be beneficial to include the effect of different compaction methods and specimen sizes on the curing mechanism, referring to varying water contents, densities and air voids.

- A more substantial economic study must be performed to determine the actual costs of Ca-alginate material in CMC or in CMP, with and without cement additives, and these should be compared to those of conventional CMA.

- It was observed that some capsules are not broken after compacting the Marshall specimens. So, it is recommended that further research be carried to evaluate the number of capsules that have broken after compaction at different compactive efforts.

- Furthermore, it is recommended to use other laboratory compaction techniques such as gyratory or vibratory compaction to evaluate the mechanical properties of CMC material, with and without cement, at different curing times.

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Appendix A

Marshall, gyratory, and vibratory compaction test specimens were prepared in this study to evaluate the mechanical performance for the CMC materials by using the Marshall Stability test described in Section 3.2.7. It was found that the Marshall compaction test specimens had higher strength levels, as shown in Figure 1.

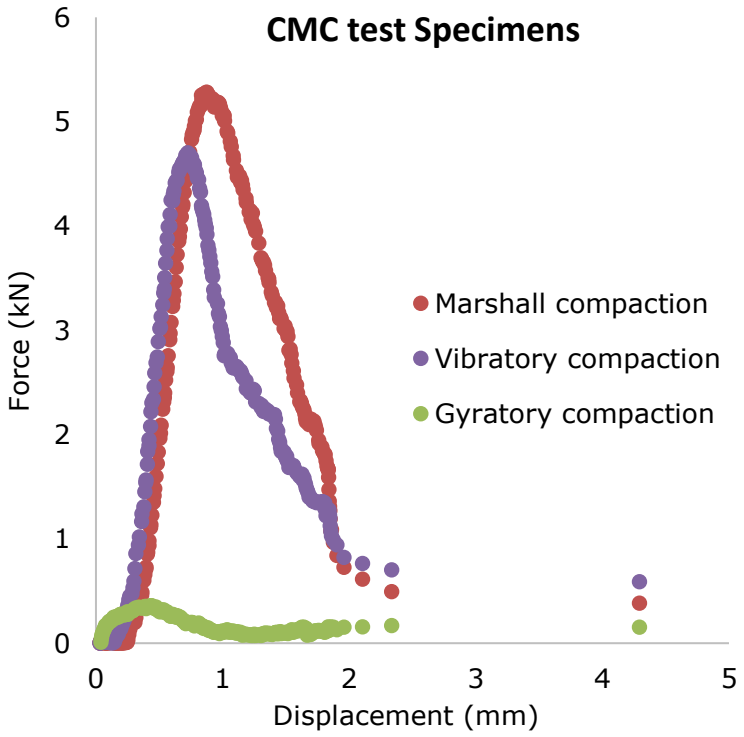

Figure 1 Marshall force registered for CMC test specimens, at 20ºC by using aggregate gradation in Table 3.1, after 24 curing.

Appendix B

- The aggregate gradation as shown in Figure 3.1 was limestone aggregates obtained from Tunstead Quarry, Derbyshire, UK, which designed based on Cooper's revised Fuller formula as shown below

$$P = \frac{(100-F)(d^n-0.075^n)}{D^n-0.075^n} + F \quad (1)$$

Where P is percent material passing sieve size d (mm), D maximum aggregate size (mm), F filler percentage and n, an exponential value that dictates the concave nature of the gradation line. The n value used was 0.45 which is an exponential factor that can be used to produce good aggregate packing. The value selected for D was 14 mm and F was equal to 4 percent.

- The aggregate gradation as shown in Figure 4.1 was also limestone aggregates obtained from Tunstead Quarry, Derbyshire, UK and consisted of the following nominal sizes: 14mm, 10, 6, dust and a few microns of filler.

By comparing the aggregate gradation in Figure 3.1 to Figure 4.1 by the CMC test specimens, it was found that

- CMC specimens did not affect any large in strength with number of blows, after 24h curing, at 20ºC as shown in Figure 2(a).
- CMC specimens also did not affect any large in strength, at different curing times, at 20ºC as shown in Figure 2(b).

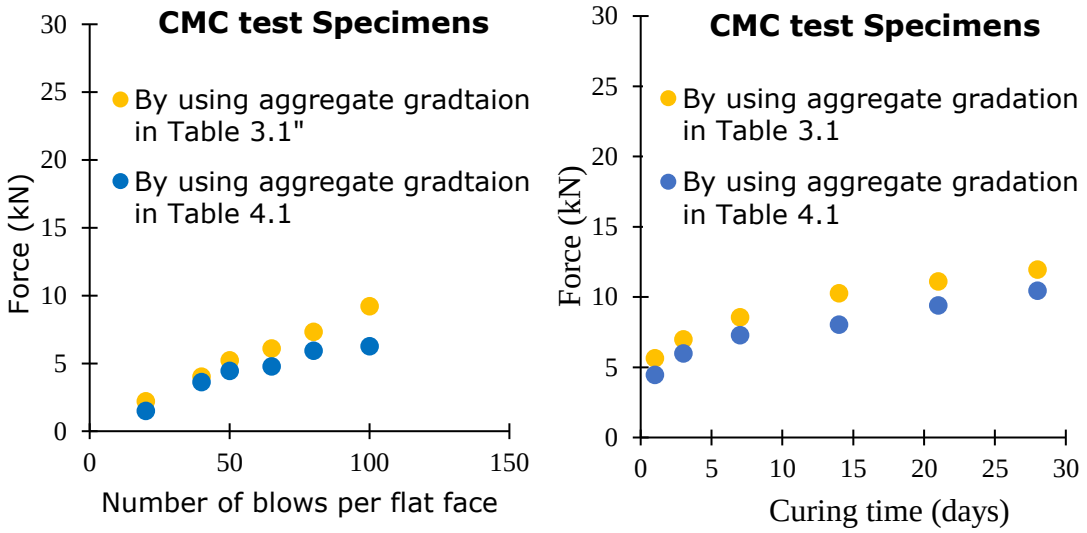

Figure 2 Marshall force registered for CMC test specimens, , at 20ºC by using aggregate gradation in Table 3.1 and Table 4.1 (a) at different number of blows per flat face, after 24 curing, and (b) at different curing times.