STUDY THE EFFECT OF CHITOSAN AS AN EMULSIFIER AND AS AN ADDITIVE OVER CATIONIC BITUMEN EMULSION

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DECLARATION

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ABSTRACT

Chitosan has amine and amino groups which have the ability to generate cationic type surfactants when combine with H+ ions. Thus its action as a cationic emulsifier is suitable for negatively charged siliceous aggregates used for road paving in Sri Lanka. This study consisted of two parts. Firstly, water soluble Chitosan was tested for suitability of using as an emulsifier in the production of cationic bituminous emulsions and secondly Chitosan was used as an additive to mix with bitumen emulsion. In the first part, currently using amine emulsifier was replaced at 20% intervals and tested for emulsion properties; emulsion viscosity, storage stability, settlement test, sieve test and breaking of emulsion. In the second part, Chitosan was added to emulsion and viscosity, storage stability and break time were tested. Results of first part indicated that Chitosan replacement was only possible up to 10% replacement for cationic slow setting type of emulsions but rheological properties of rapid setting emulsions could be improved by replacing up to 60% of amine emulsifier with Chitosan. A significant increase in viscosity from 16 SSU (with 0% Chitosan) to 43 SSU (with 60% Chitosan) was observed for rapid setting emulsions. Storage Stability showed the optimum value of zero at 40% replacement and all the values up to 60% replacement were found to be within the ASTM specified level of ±1%. Break time measurements suggested that for slow setting type emulsions Chitosan use as an emulsifier has increased the emulsion breaking rate. Further high viscous and stable rapid setting emulsion could be obtained without hindering the compliance to ASTM standard by replacing the amine emulsifier with Chitosan. Results of second part suggested that Chitosan acts as a viscosity modifier and increases the emulsion viscosity from 26SSU to 92SSU when added at 0.2% of emulsion weight. But this addition has increased the settling tendency of emulsion thus most suited to be mixed at the point of use. In both cases, at a critical amount of added Chitosan was observed. This maximum limit was found to be 0.2% (w/w).

Key words: Chitosan, Bitumen Emulsion, Viscosity Modifier

DEDICATION

I dedicate this thesis to my father who could not see my achievements in his life and to my mother who has brought me thus far on her shoulders.

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LIST OF ABBREVIATIONS

Abbreviation	Description
ASTM	American Society of Testing and Materials
CPC	Ceylon Petroleum Corporation
CRS	Cationic Rapid Setting
CSS	Cationic Slow Setting
DD	Degree of Deacetylation

LIST OF APPENDICES

1.0 Introduction

1.1 Bitumen Emulsion

Bitumen emulsion is a widely used material in the road maintenance work. It is an environmentally friendly material and also an energy saver as it does not need heating which emits pollutants and consume energy. Use of bitumen emulsion is introduced in the early twentieth century as a dust controlling method. This has extended its use as environmental concerns have arisen against using hot bitumen due to emission of volatile organic matter.

Figure 1.1: Application of Bitumen emulsion

Bitumen emulsion is manufactured using a colloidal mill to provide a high shear action. An emulsifier is added to lower the interfacial tension between two immiscible phases of bitumen and water in order to make them miscible. Emulsion can also be produced using a homogenizer.

Sri Lanka has started using bitumen emulsion for its road maintenance work in the mid 1980’s. In Sri Lankan context it is commonly used for applications like cold mix, priming, tack coat and sand sealing (Institute for Construction Training and Development [ICTAD], 2009).

Different types of bitumen emulsion are available in the industry. Basic categorization depends upon the surface charge of the bitumen droplets and it can be either anionic or cationic. In Sri

Lanka cationic emulsions are mostly used due to the negatively charged aggregates (ICTAD, 2009).

Currently several different emulsifiers are being imported to Sri Lanka. All of these emulsifiers are produced from natural sources. With the increase in processing cost and demand for natural resources for other applications, cost of these emulsifiers has risen significantly in the recent past. Even though the percentage of emulsifier in the bitumen emulsion is very low their cost element is significant as depicted in Table 1.1. Considering the volume of emulsion needed for the rapidly developing road network it is uttermost important to find a suitable emulsifier based on resources available in Sri Lanka.

Table 1.1: Emulsifier volume and cost elements in percentages

Type of emulsion	**Volume percentage of emulsifier (%) per liter of emulsion**	**Cost percentage of emulsifier (%) per liter of emulsion**
Cationic Slow Setting	0.9-1.2	6-9
Cationic rapid Setting	0.2-0.3	2-3

Source: Published with the permission of Maga Neguma Emulsion Production Company (2013)

Reviewing of the structure and functionality of the presently used emulsifiers suggest that the replacing surfactant must preferably have amine groups to form as cationic heads and a counterpart which can connect to the bitumen droplet. One such locally available material is Chitosan.

1.2 Chitosan

Chitosan can be economically extracted from crustacean shells which are otherwise is a waste in fishing industry. Sri Lanka is having 1,340 km long coastal area and as per year 2005 it has crustacean crop of about 5000t (National Aquaculture Development Authority of Sri Lanka [NADA], 2005). Therefore Sri Lanka has a great potential of producing Chitosan generating from the otherwise dumped waste crustacean shells.

Chitosan has the desired amine groups since it is a deacetylated version of Chitin (Pillai, Paul and Sharma, 2009) and has the proven potential of emulsification (Rodriguez, Albertengo and Agullo, 2001). Chitosan is used in multiple industries such as water treatment, food, agriculture, cosmetic etc. World production of Chitosan is 13,700t in the year 2010 (Cosgrove, 2012).

Chitosan has been successfully used as an emulsifier in oil-water emulsion systems of paraffinic oil in aqueous solutions. However use of Chitosan as an emulsifier for bitumen emulsion is yet to be explored. Therefore this research work can be considered as a starting point which will open up the path to many future research works.

1.3 Aim and Scope

Scope of the present work is to identify Chitosan as a potential source for making bitumen emulsion.

Aim of this research is to study the effect of Chitosan as an emulsifier in the production of cationic bitumen emulsion and also to evaluate the effect of Chitosan as an additive to bitumen emulsion.

1.4 Thesis Outline

This thesis consists of five chapters which are set in order to cover the aim of the research work with their own introductions and descriptions. First chapter described the justification of research work with reference to research background. The aim and scope is also given.

Earlier studies of bitumen emulsion and its constituents, Chitosan chemistry and its applications and various theories required to explain the emulsion behavoiur are presented in Chapter 2.

All materials and methods used for this research work are given in Chapter 3. This chapter also reveals how this research project is conducted together with conditions maintained during the test and emulsification instruments used for the same.

Results are discussed in Chapter 4 with elaboration using graphs and analysis using various theories and compliance of the emulsion with respect to the ASTM standard. Chapter 5 describes the conclusions made at the end and also the possible future work to attempt.

2.0 Literature Review

2.1 Bitumen Emulsion

Emulsion is the form in which two naturally immiscible liquids are in dispersion. In the case of bitumen emulsion the two immiscible liquids are bitumen and water. They are sending through a high sheer force of colloidal mill and with the addition of emulsifier, bitumen emulsion is formed.

Emulsions can be either oil-in-water (o/w) emulsions (Figure 2.1) or water-in-oil (w/o) emulsions (Figure 2.2). In addition to these major types emulsion can also be in the form of multiple layered emulsions such as o/w/o or w/o/w (Figure 2.3). Bitumen emulsions are considered as o/w type emulsion (Transportation Research Board, Washington, 2006).

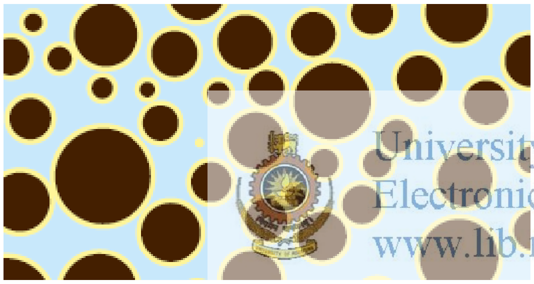


Figure 2.1: Oil in Water emulsion

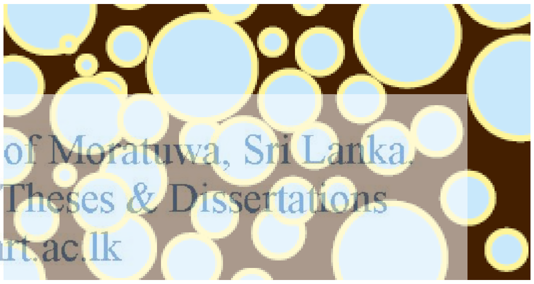


Figure 2.2: Water in oil emulsion

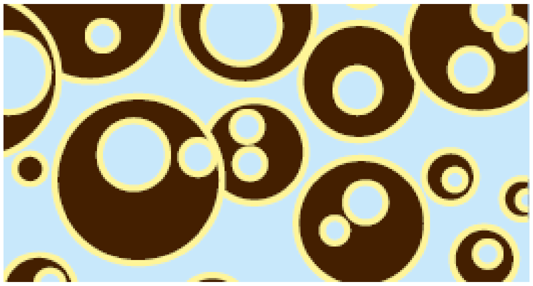


Figure 2.3: Multiple W/O/W emulsion

Bitumen emulsion was first developed in 1923 (Bouteiller, 2010) and was used as a spray application for the purpose of dust controlling. It is used as an alternative to the cut back bitumen which is a mix of bitumen and kerosene. Environmental concerns regarding the emissions from cut back bitumen is used has promoted the use of bitumen emulsion. Especially volatile organic compounds emit from cut back bitumen could be prevented by using bitumen emulsion (Products Division, Chemical Sectors directorate Environment Canada, 2012).

Bitumen emulsion can be categorized as anionic and cationic based on the charge of the droplets. It can also be categorized by considering the set time of the emulsion (Asphalt Institute and Asphalt Emulsion Manufacturers Association [AEMA], 2001). According to set time classification it is of four major types.

(a) Slow Setting
(b) Quick Setting
(c) Medium Setting
(d) Rapid Setting

Slow Setting and quick setting type of emulsions show the most delayed setting and thus they give enough mix time with aggregates. Such delay in setting time is required for applications such as pre coated chips and dense graded plant mixes (Salomon, 2006). Generally slow setting type of emulsions use higher dosage of emulsifier than in other type of emulsions. Emulsifiers for slow setting type emulsions mostly contain poly ammonium salts. Such emulsifiers are regarded as more stable and they delay the breaking process.

Quick setting (QS) type emulsions set faster than slow setting but they still provide enough time to mix with aggregate before setting. These types of emulsions are desired in applications of slurry sealing and micro surfacing where such shortened set time is required. Cationic Quick Setting type emulsions are produced with emulsifier of amidoamine with the dosage of 1.5-2.5 percent of emulsion weight (Levin, 2003)

Cationic medium setting (CMS) type emulsions are made from tallow diamine and it is used in applications where set time can be of few minutes. Aggregates used to mix with CMS are coarse aggregates having significant amount of voids thus a higher viscosity is required to prevent emulsion run off between those voids. CMS emulsions are having the required high viscosity.

Rapid setting types are designed for applications which require faster setting. Most of such applications are surface applications and emulsifiers used to produce this type of emulsions are fatty amines like diamine, imidazolines, amidoamines etc. These amines become soap when acid like hydrochloric is mixed.

2.1.1 Bitumen Emulsion Applications

Bitumen emulsion is applied on multiple applications in road maintenance work. Surface applications such as sand sealing and chip sealing are formed using cationic rapid setting type emulsions as they require faster setting in order to open roads to the traffic quickly. In contrast cold mix is an application which requires mixing with aggregate thus needs slow setting type emulsions to provide enough mixing time. Tack coating uses slow setting type emulsion as it provides a bond between asphalt layer and the aggregate (Salomon, 2001).

2.1.2 Emulsification Process

Manufacturing of bitumen emulsion is the process of mixing two immiscible liquids together. Those two liquids are bitumen and water. It needs energy to overcome the energy barrier preventing their mixing. In the emulsification process, this energy is provided by the colloidal mill and emulsifier. Colloidal mill provides the mechanical energy and emulsifier provides physiochemical energy which lowered the surface energy by chemical interactions. Figure 2.4 depicts the major components of emulsion plant.

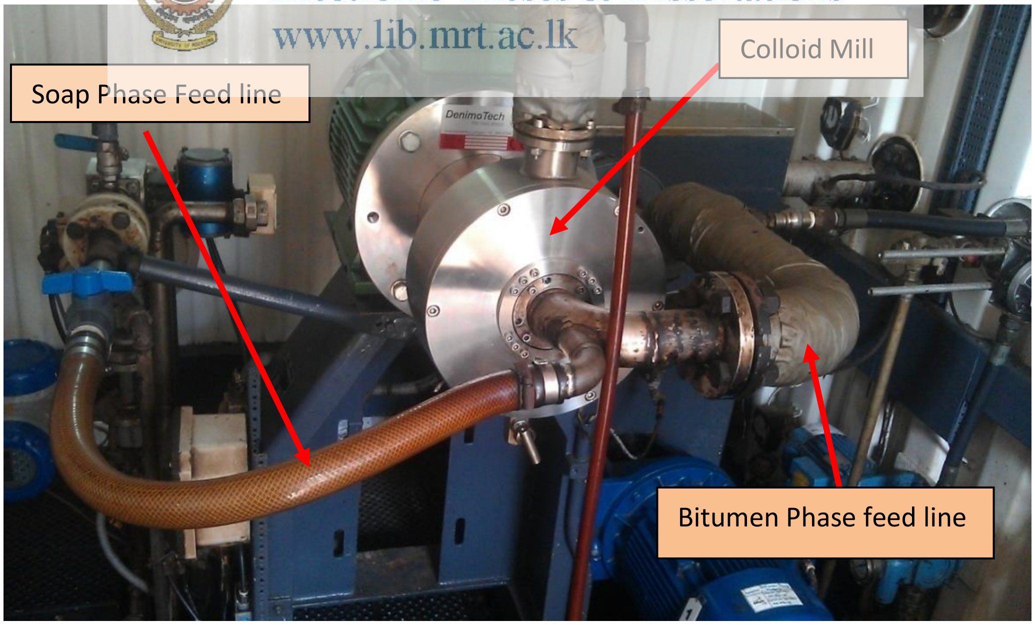


Figure 2.4 Colloidal mill

Source: Maga Neguma Emulsion Production Company (Pvt) ltd

Manufacturing of bitumen emulsion can be done either batchwise or continuously. This categorization is based on how two liquids are fed to the colloidal mill. Bitumen is fed together with kerosene to reduce the viscosity of the bitumen phase. This viscosity reduction eases the shearing action at the colloidal mill. Water phase is fed as a mixture of water, emulsifier, stabilizer and acid (Figure 2.5). Two phases are mixed together in the mill and high shear action together with emulsifier form tiny droplets of emulsion possibly in the size range of 1-20 microns (Furlong, James, Kalinowski and Thompson, 1998).

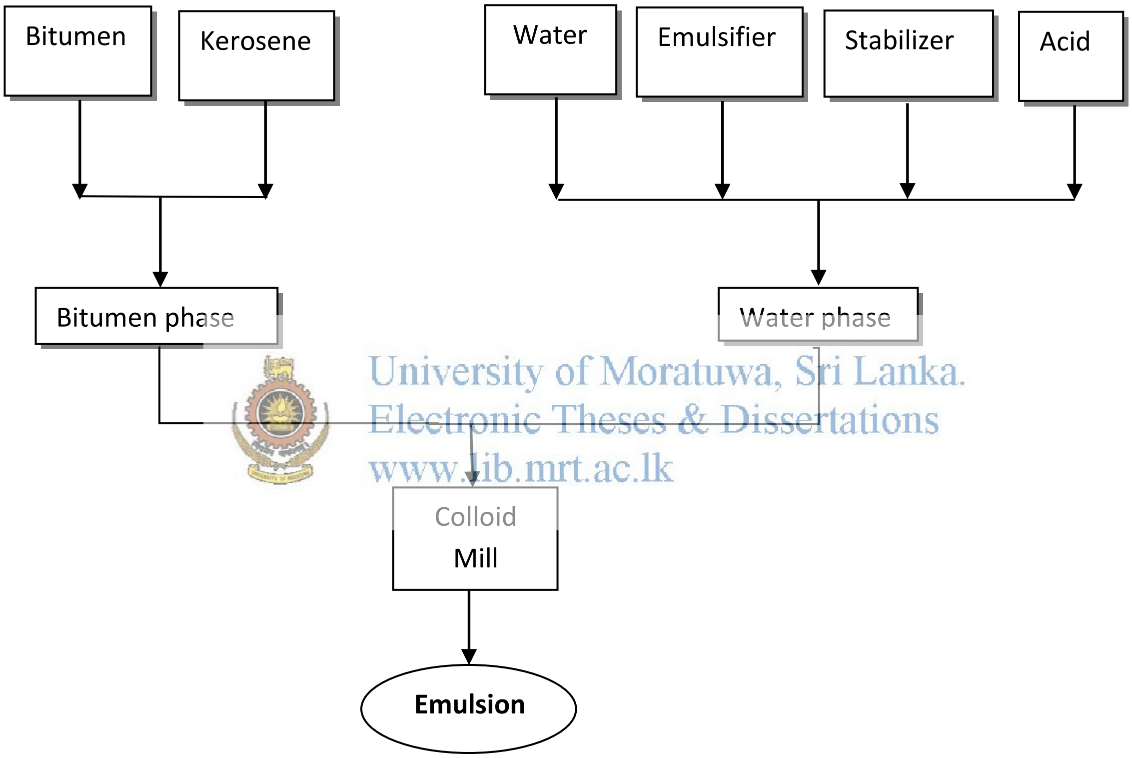


Figure 2.5: Flow Chart of Emulsion manufacturing process

2.1.3 Raw materials

2.1.3.1 Bitumen

Bitumen consists of a wide variety of reddish brown to black viscous liquids or semi solids, which contains high molecular weight hydrocarbons and has adhesive properties. The terms Bitumen and Asphalt are used interchangeably to call this same liquid. Americans use the term Asphalt and the term Bitumen is used by others. Bitumen can either be manufactured from petroleum crude oil or it can be extracted from natural asphalt deposits (Read & Whiteoak, 2003).

The American Society for Testing and Materials (ASTM) defines bitumen as a generic class of black or dark colored (solid, semi-solid or viscous), cementitous substances, natural or manufactured, composed principally of high molecular mass hydrocarbons of which asphalts, tars, pitches and asphaltenes are typical.

Chemical composition of bitumen would vary depending upon the source of crude oil extraction and the processing method of extracting the bitumen from crude. But in overall its structure predominantly comprises of hydrocarbons. In addition to the hydrocarbons bitumen also contains elements such as Nitrogen, Oxygen and Sulfur. Approximated percentages of the elements present in bitumen are as in Table 2.1 (Read & Whiteoak, 2003).

Table 2.1: Elemental composition of bitumen

Element	**Composition %**
Carbon	82 - 88%
Hydrogen	8 - 11%
Sulphur	0 - 6%
Oxygen	0 - 1.5%
Nitrogen	0 - 1%

Bitumen is considered to have two main components, asphaltene and maltene. Maltene can be further divided as saturates, aromatics and resins. The asphaltene is dispersed in the maltene medium as shown in Figure 2.6 (Bearsly, Forbes & Haverkamp, 2004).

Asphaltenes are responsible for increasing or decreasing the viscosity of the bitumen. These aromatics have high molecular weight and high polarity. Their chemical structures consist of hydrogen, carbon, sulfur and nitrogen and the percentage of asphaltene is in the range of 5-25% of bitumen.

Resins are having less molecular weight with compared to asphaltenes and having low percentages of oxygen, nitrogen and sulphur. They are having a polar structure and exhibit strong adhesive nature. Aromatics are the major constitute in bitumen as they contain about 40-65% of bitumen. Non polar carbon chains with unsaturated aromatic rings are present in their structures. Saturates are the non polar chain hydrocarbons with some aromatic rings present in the chain (Read & Whiteoak, 2003).

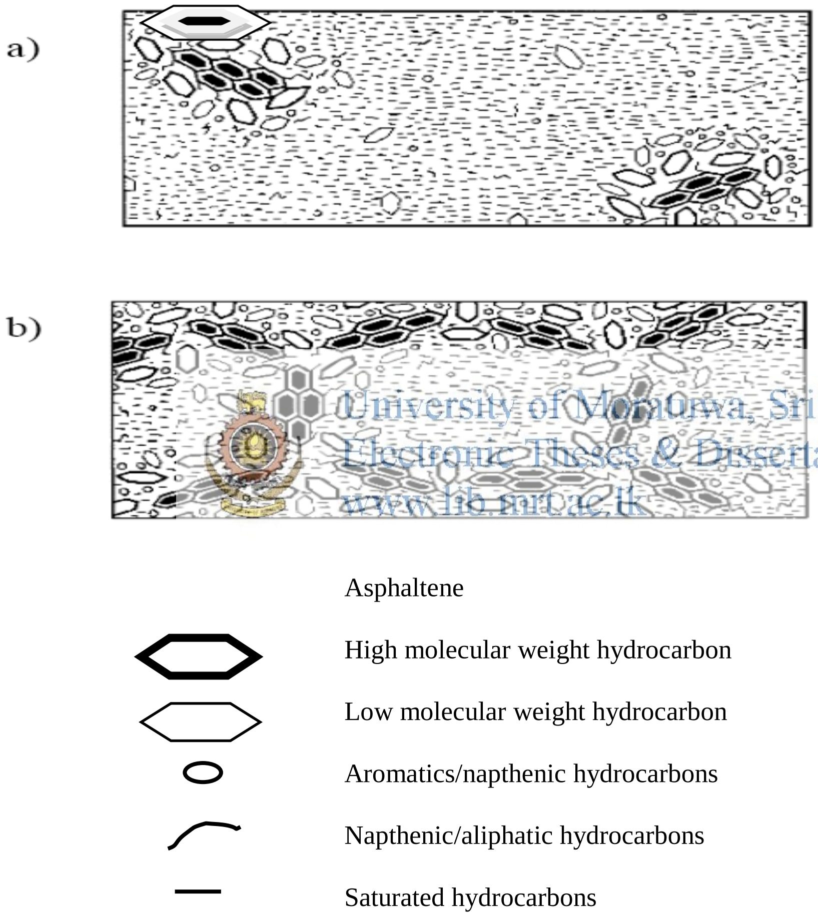


Figure 2.6: Aspahltene dispersed in Maltene

Source: Shell Bitumen Handbook, 2003

2.1.3.2 Water

Water is the continuous phase in bitumen emulsion in which bitumen droplets are dispersed. It contributes as the second highest ingredient in the emulsion composition. Water should not carry impurities as it can adversely impact the quality of the emulsion. If ions are present in water it can influence the charged nature of the emulsion droplets.

Water heating at some instances is required if emulsion temperature is in the range of 75°C-85°C.

2.1.3.3 Emulsifier

Emulsifier is the most important component in the emulsification process as it creates a charged surface which prevents particle agglomeration. It acts as the surfactant and reduces the interfacial energy between bitumen and water. Emulsifiers are produced from natural sources such as vegetable oils and animal fats. Depending on the surface charge emulsifiers can either be cationic or anionic (Asphalt Institute, 2001).

Anionic emulsifiers are made by mixing fatty acids and sodium hydroxides as follows.

$RCOOH + NaOH \rightarrow RCOO^- + Na^+ + H_2O$

This creates a negatively charged group $RCOO^-$ when in emulsion that $RCOO^-$ group imparts negative charge to the surface of bitumen droplet. Anionic emulsifiers are used in road construction industry to mix with carbonaceous aggregate as surfaces of such aggregates carry positive charge due to calcium ion.

Cationic emulsifiers are having nitrogen as the main element of creating cationic head due to its unshared electron pair. Compounds such as fatty amines, polyammonium salts, imidoazolines, amidoamines contain such nitrogenous compounds. Unshared electron pair of Nitrogen can attract protons provided by hydrochloric acid and form a positively or cationically charged head group as follows (Levin, 2003).

$RNH_2 + HCl \rightarrow RNH_3^+ + Cl^-$

Cationically charged particles repel each other in the case of cationic emulsions. Such types of emulsions are used to mix with siliceous aggregates which have silanol groups that impart negative charge to the surface. Cationic type emulsions are the most commonly used emulsions and in Sri Lanka this is the only type of emulsion in use.

Emulsifier is the element which decides the setting time of the emulsion. Cationic slow setting type emulsions mainly use polyammonium salts (Figure. 2.7) while cationic rapid setting type emulsions use diamines (Figure. 2.8). Polyammonium salts have permanent cationic group as the Nitrogen molecule is tertiary Nitrogen. Therefore they don't require addition of acid to turn the emulsifier into the cationic nature. In contrast rapid setting type emulsions need addition of acid to provide proton on to the nitrogen present in them (Asphalt institute, 2001).

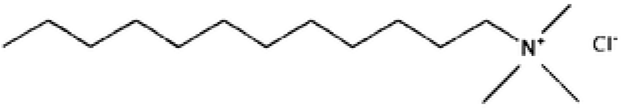


Figure 2.7: Polyammonium Salts

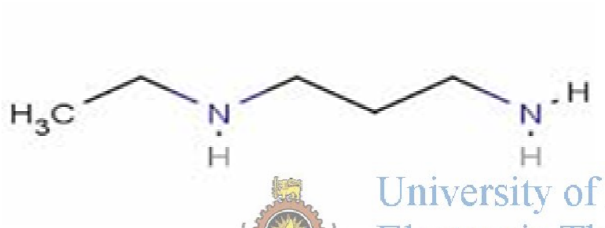


Figure 2.8: Diamines

As per the Bancroft rule, emulsifier impacts the decision of continuous phase and dispersed phase. Phase in which emulsifier is more soluble is the continuous phase (Bancroft, 1913). If the emulsifier is soluble in water, water is the continuous phase while oil is the dispersed phase and vice versa. In other words it decides whether the emulsion is oil in water (O/W) type or water in oil (W/O) type emulsion.

2.1.3.4 Acid

In the process of manufacturing bitumen emulsion it uses hydrochloric acid to maintain the pH in the soap solution. pH value determines the cationic or anionic nature and also the zeta potential of the emulsion. As described in section 2.1.3.3 cationic rapid setting emulsifiers require acid to form cationically charged head groups. On the other hand, cationic slow setting emulsifiers have permanent cationic groups, pH can be maintained at comparatively higher value. Therefore emulsifiers used for rapid setting type emulsion need acid to convert in to cationic type while slow setting type doesn't need acid addition (James & Wates, 1993).

2.1.3.5 Calcium chloride

Bitumen contains salts retained after improper desalting of crude. In the presence of such salts water goes inside the bitumen droplets in the emulsion and droplets swell subsequently. This will increase the viscosity since particle size is increased due to swelling. But as the time passes this water releases and viscosity drops. If this happens, emulsion viscosity shows a fluctuation which is not acceptable. Presence of Calcium Chloride in the emulsion reduces the water osmosis to the bitumen droplets and that maintains the viscosity at a consistent level (Furlong, James, Kalinowski & Thompson, 1999). Calcium Chloride also increases the density of the water phase of the emulsion and it contributes to prevent settlement of bitumen droplets which have higher density than water. Thereby it performs the function of stabiliser as well.

2.1.4 Emulsification Equipment

Main equipment required for manufacturing bitumen emulsion is the colloid mill which provides mechanical energy through a high shear force. Rotational speed and mill gap of the colloid mill decide the particle size of the emulsion. Therefore it also impacts the physical properties like viscosity. Typical speeds of the colloid mill for manufacturing of bitumen emulsion are in the range of 2000-6000 rpm and mill gap is kept in between 2.0-2.5 mm. In addition to that storing tanks for raw materials and products, pumps, parameter measuring equipments and control panel with displays are also included in the manufacturing plant. Heating facility is available in some plants to heat the water if required.

2.1.5 Emulsion Breaking and setting process

Emulsion breaking and setting for Cationic type emulsions is the process of colloid particles of bitumen reverting back to a continuous bitumen phase. There are four stages in the whole process. First stage is the destabilization of emulsion which causes colloid particles get closer. Second step is the flocculation of those particles that make them agglomerate after emulsifiers are absorbed by the aggregates. These two steps together called as the breaking of emulsion. After flocculation, bitumen droplets form a continuous film which is considered as the coagulation which is the third step. In final step, water evaporates allowing base binder adhered completely (Hanz., Arega & Bahia, 2008). These four steps are graphically shown in Figure 2.9.

Hefer & Little (2005) described the adhesion between bitumen and aggregate under four theories. That model can be used to explain the emulsion breaking and setting mechanisms and respective times as follows.

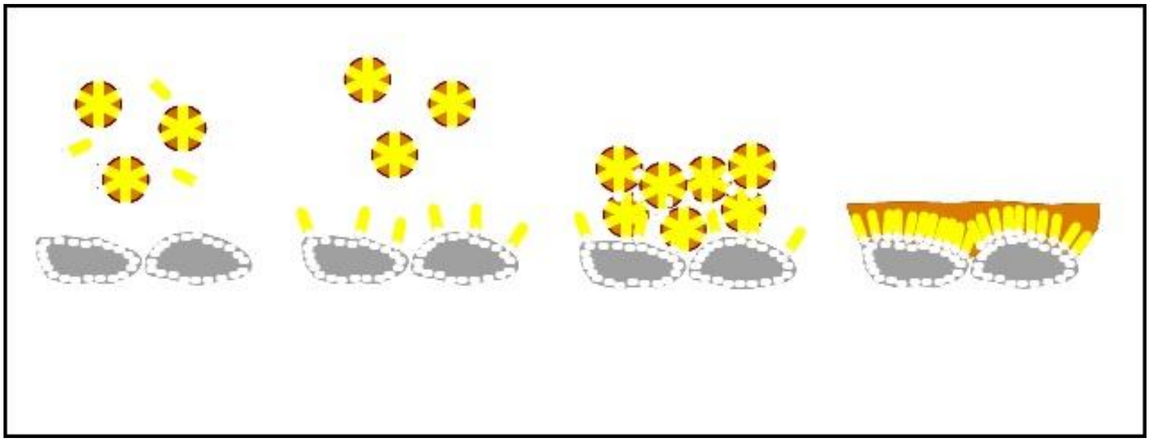


Figure 2.9: Possible stages in the setting of a cationic emulsion

Source: Transportation Research Circular No E-C102, Transport Research Board (U.S), 2006

2.1.5.1 Electrostatic Theory

Aggregate surfaces can be characterized either as electropositive or electronegative. It is considered that in the presence of water many surfaces show either positive or negative charge. Such charges create an electric field thus they are attracting counter ions.

Colloid particle become ionic when its surface attracts some charged groups and attached them to the surface. This can happen under different methods such as ionization of surface groups, ion adsorption, ion dissolution and ion substitution (Fermin & Riley, 2010). Charges attached as such create a layer of electrical charges. This layer consists of two sub layers namely Stern layer and diffuse layer (Figure 2.10). Stern layer is the inner layer to which charges are strongly bound and the diffuse layer is the outer layer which consists of weakly attached charges

Diffuse layer has a boundary in which charges inside that move along with the particle and charges beyond that don’t move with it. This boundary is called as slipping plane and the potential at that boundary is called as zeta potential (Butt, Graf & Kappl, 2004).

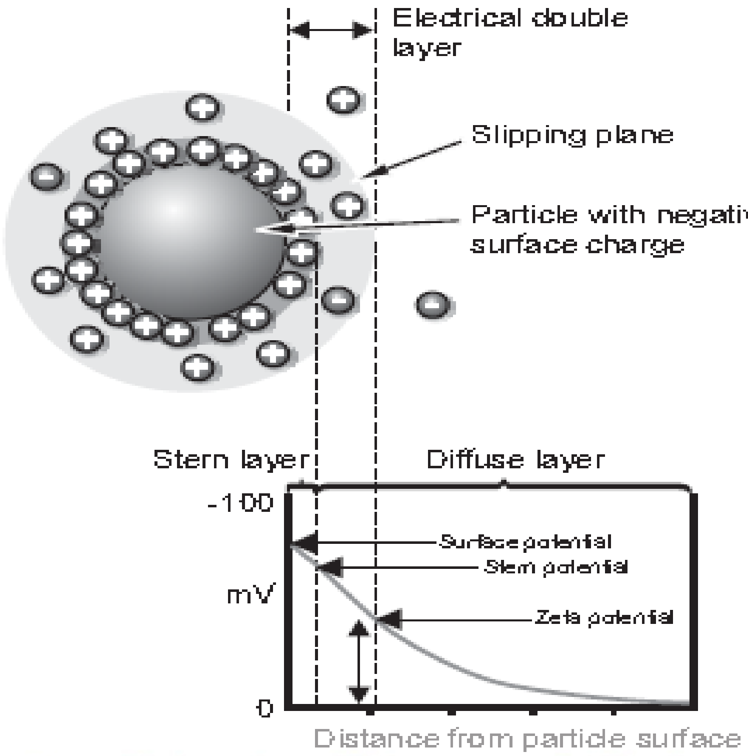


Figure 2.10: Electrical Double layer around a particle

Source: Malvern Instruments Ltd.

When zeta potential is high it implies that the charge density around the particle is high. This attributes to a stable dispersion of colloid particles since repulsion force between the particles is high. On the other hand colloid systems with lower zeta potential tend to show less stability (Dybaiski, 1976).

Zeta potential strongly depends upon the pH of the solution. pH value is the factor deciding the significance of the zeta potential for the stability of a respective solution.

Assume a particle in suspension with a positive zeta potential. If more acid is added to this suspension then the particles will tend to acquire a more positive charge. If alkali is then added to this suspension a point will be reached where the positive charge is neutralized. Any further addition of alkali can cause a buildup of negative charge. Therefore a zeta potential at low pH will be positive and at high pH it will be negative (James & Wates, 1993).

Applying this zeta potential theory to bitumen emulsion systems can be interpreted as follows. Hydrophobic tail group of emulsifier is lagging inside the bitumen droplet and its hydrophilic head is keeping at outside of the droplet. Some emulsifiers are having head groups which are turned ionic when acid or base is added while others are having permanent charged groups. Thus it allows creating a net charged surface surrounding the particle. Charged emulsion droplets repel each other and retain the stability of the system.

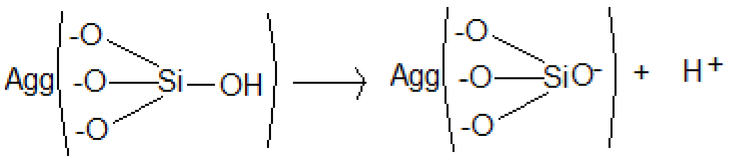
When emulsion is applied on aggregates it adheres on to the aggregate by the mechanisms described under emulsion breaking and setting process. Rapid setting type emulsions breaks faster than slow setting type emulsions and rapid setting emulsions are manufactured at lower pH while slow setting emulsions are produced at relatively higher pH values (James & Wates, 1993).

Hefer and Little describes the interaction between bitumen and aggregate under electrostatic theory as follows. Calcium Carbonate ($CaCO_3$) comprising aggregates are called limestone and they carry electropositive surface charges. When such aggregates are fractured, newly formed surfaces contain ionic charges of Calcium and Carbonates. When aggregate is crushed leaving unsatisfied charges on its surface it attracts water and subsequent adsorption of carbon dioxide on to the surface water. Finally aggregate surface forms an electropositive charge as follows.

$$(AggCaCO_3H) \longrightarrow (Agg\text{-}Ca^+) + (HCO_3^-)$$

Agg represents the bulk aggregate structure and HCO_3^- is weakly bonded to Calcium ion as weak base. Therefore these types of surfaces are behaving as electropositive surfaces.

In contrast to limestone, aggregates such as quartzite and granite form electronegative surfaces once fractured. With the adsorption of water on to such aggregate its surfaces turn to electronegatively charged nature as follows.



Depending on the negative or positive charge on the aggregate surface it attracts oppositely charged droplets when applied on to its surface. The difference in electronegativities between aggregate and colloid particles is the driving force behind such attraction.

2.1.5.2 Chemical Bonding Theory

Major constituents of bitumen emulsion are bitumen, water and emulsifier. Bitumen molecules are non-polar long chain hydrocarbons and aromatic rings which are saturated with hydrogen. Such hydrocarbons are mainly interacting through Van Der Waals forces and it creates bonds with hydrophobic non-polar groups of emulsifier. Emulsifiers used for cationic type emulsions are di-amines or quaternary ammonium salts. Ionic head groups of emulsifiers are hydrophilic thus tend to keep inside the water. Tail groups are hydrophobic so they would keep inside the bitumen droplets. Therefore bitumen as the adhesive material between aggregate, contains ionic functional groups that can form chemical bonds with aggregate.

Aggregates are having a uniform chemical composition where atoms are formed in a certain order. When the aggregate is crushed, they form unsatisfied charges on the surface as explained in the electrostatic theory. Those charges act as the reactants which are reacting with functional groups of emulsion such as hydrophilic head groups of emulsifier.

2.1.5.3 Mechanical Theory

Mechanical theory describes the impact of physical nature of aggregate on adhesion. Under this theory it describes several mechanical effects through which adhesion occurs. One such effect is called as lock and key effect where adhesive liquid travel into the pores of the aggregate and anchoring inside them. Another effect is from the surface roughness which increases the adhesion by increasing surface area.

2.1.5.4 Thermodynamic Theory

Thermodynamic theory is about the energy changes in the system. In emulsion-aggregate systems bitumen droplets carry a surface energy due to the presence of emulsifier in their surfaces. This can be considered as the potential energy of emulsion. Due to the opposite charge between emulsion and aggregate they are attracted to each other. As the distance gets closer, potential energy reduces and settles to a lower energy state which is more stable. Lowering of energy is indicated by negative Gibb's free energy.

2.2 Chitosan

Chitosan is extracted from exoskeleton of the crustaceans such as prawns and crabs. Crustacean shells are a waste in fish industry (P.K.Dutta, Dutta and Tripathi, 2004). Thus it is considered as an underutilized resource. Chitin which is the product derived from those shells. It is considered as the second mostly available natural polysaccharide after cellulose (Puvvada et al., 2012). Chitin structure is only varying from cellulose by one hydroxyl group in cellulose replaced by acetamide group (Kim, 2004).

As per US patent publication number 8318913 B2, Chitosan manufacturing process starts with the demineralization of crustacean shells to remove Calcium Chloride and Calcium Carbonate by hydrochloric acid solution. Resultant chitin is deproteinated using 4-6 % concentrated NaOH at temperature of 70-80°C. Chitin remained after deproteination step is deacetylated using 40-50% NaOH solution at 100-200°C.

Important parameter of the selected Chitosan is the degree of deacetylation (DD). DD value is given as a percentage value which is the percentage of amine containing groups in the structure. If the structure contains more amine groups than amine acetyl or if DD value is greater than 50%, it is considered as Chitosan. If the structure contains more amine acetyl groups or if DD value is less than 50%, it is considered as Chitin (Figure.2.11). Rodriguez et.al (2001) suggested that Chitosan molecules with high DD values promote the formation of oil in water emulsions while lower DD values promote the formation of water in oil type of emulsions.

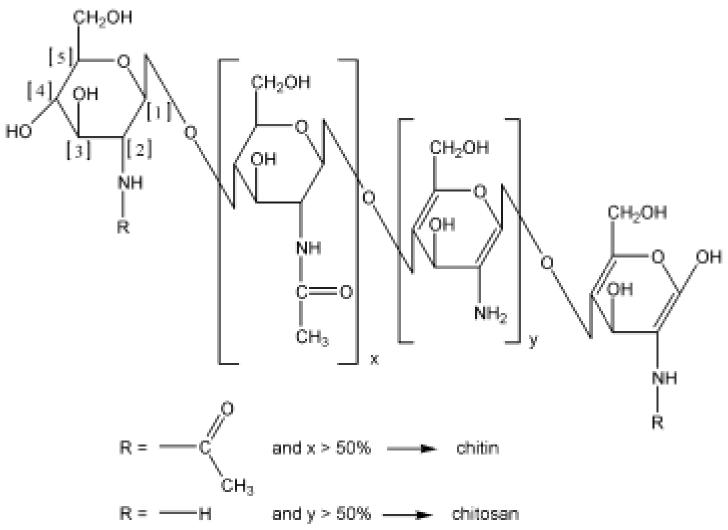


Figure 2.11: Chitin and Chitosan Structure

Source: Elsevier, Progress in Polymer Science 34 (2009) 641‑678

2.2.1 Chemical Properties of Chitosan

Chitosan structure (Figure.2.12) consists of methylol, oxo, amine acetyl and amine groups as active groups. Due to the presence of amine group, Chitosan forms a cationic molecule when reacted with acids and also shows increased water solubility than Chitin (Pillai et, al., 2009). Chitosan is turned to readily water soluble by certain chemical modifications. One such method is presented by Cho et.al (2011) which describes that Chitosan is reacted with epoxy group containing moieties. This gives a Chitosan derivative which has a tertiary amine group which is readily ionic (Figure.2.13).

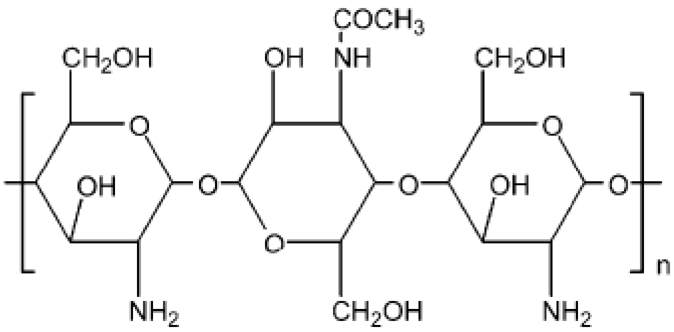


Figure 2.12: Chitosan Structure

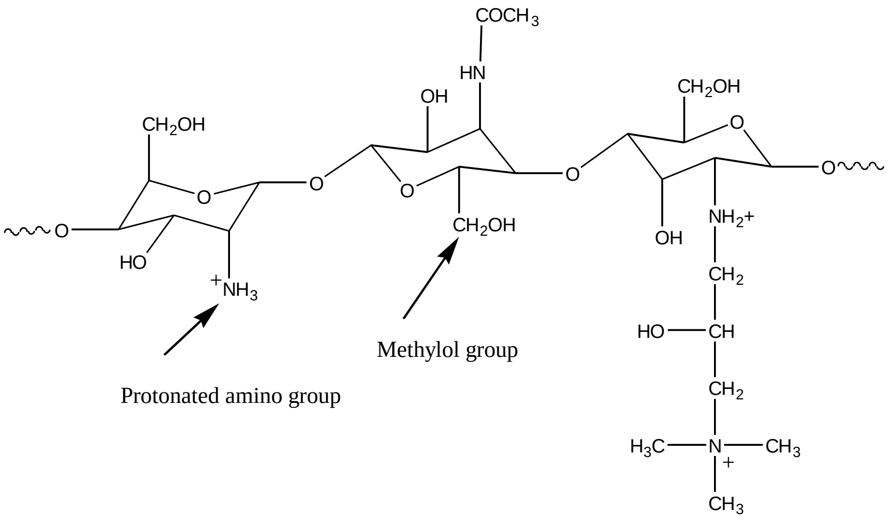


Figure 2.13: Cationic form of Chitosan

Due to the amine group in Chitosan it follows the typical reactions of amines such as N-acylation and Schiff reaction. When reacted with ketones and aldehydes this amine group forms ketimines and aldimines, respectively.

Methylol, oxo and amine acetyl groups are each responsible for undergoing reactions which are unique for each group. Thus Chitosan has a potential of showing multiple characteristics depending on which group is reacting.

2.2.2 Applications of Chitosan

2.2.2.1 Water Treatment

With the presence of proton attracting groups such as amine, Chitosan shows a polycationic character. Due to this nature it is used as a flocculent as it agglomerates anionically charged waste materials and forms flocs. Weltroswki et al. (1996) has used N-benzyl sulphonate derivative of Chitosan to remove metal ions from an acidic medium thus it has the potential of chelating metal ions.

2.2.2.2 Food Industry

Food industry uses Chitosan as a stabilising agent in the form of microcrystalline Chitosan due to its emulsification capacity, thickening and gelling effect (Dutta et al., 2004). It also uses as an antimicrobial film to apply as an eatable coating (Leceta, Guerrero & Ibarburu, 2013).

2.2.2.3 Agricultural Industry

Naeem M. Hassan et al. (2010) revealed the applicability of Chitosan as a plant growth enhancer and a biopesticide which would improve the self defence from fungal infections. It also proved its ability in promoting germination and sprouting.

2.2.2.4 Cosmetics

P.K.Dutta et al. (2004) presented the applications of Chitosan in cosmetic industry as follows. Chitosan is in the class of hydrocolloids, but it is the only natural cationic gum. Its viscosity increases when neutralised with acid. This eases the interaction with Chitosan and hair or skin. Chitosan is carrying a positive charge while hair is negative. Therefore when Chitosan containing solution is applied on hair it would create a film which increases the smoothness and softness of hair.

2.2.3 Emulsification potential of Chitosan

Chitosan is an amino polysaccharide which has the proven potential of converting in to cationic type emulsifier when combined with acid. Some research works suggest that Chitosan performs the emulsification as an emulsifier when co-exists with another emulsifier. There were number of studies being performed by scientists to use Chitosan alone as an emulsifier.

Rodriguez, Albertengo & Agullo (2001) studied the emulsification capacity of Chitosan in sunflower oils. In that study they have used acid dissolved Chitosan samples with of 75%-95% Degree of Deacetylation at concentration range of 0.5% to 2%. Their results suggested that Chitosan has successfully formed w/o/w emulsion which is stable and their viscosities were proportional to the Chitosan concentration.

Torrico, No, Prinyawiwatkul, Janes & Corredor (2011) suggested that mineral oil-chitosan emulsion could be used as a coating material on chicken eggs to improve quality and prolong shelf-life during storage.

Liu, Wang, Zou, Wei & Tong (2012) found that Chitosan has behaved effectively as an emulsifier without hydrophobic modification in oil-water emulsion systems made using liquid paraffin, n-hexane, toluene and dichloromethane. Emulsions produced in that research work has shown long term stability for more than two months.

Payet & Terentjev (2008) studied the emulsification of Paraffin oil by using Chitosan as the only emulsifier. In their study Chitosan had produced an emulsion with good long term stability by creating a polyelectrolyte brush at the phase interface.

3.0 Methodology

3.1 Introduction

This research work is mainly divided into two parts. First part is on the analysis using Chitosan as an emulsifier in the production of bitumen emulsion and second part is on using Chitosan as an additive to bitumen emulsion.

The main difference between the first and second parts of the experiments was the total amount of emulsifier (including Chitosan) was kept constant in the first part while emulsifier amount excluding Chitosan was kept constant and Chitosan amount was varied in the second part. In other words emulsifier was replaced with Chitosan in the first part while Chitosan was added on top of the emulsifier in the second part.

CSS1 and CRS1 emulsion types were selected to produce under this research as they are the most commonly used emulsion types in the road construction and maintenance work. CSS1 emulsions are used for the applications of cold mix, tack coat, priming, slurry sealing etc. Setting time is the most important property for CSS1 type of emulsions as applications using CSS1 emulsions are required to have significant time to allow mixing before set. CRS1 emulsions are used for sand sealing and chip sealing which are surface treatments. Viscosity is the most important rheological property for rapid setting type of emulsions.

3.2 Experiments for using Chitosan as an emulsifier in the production of bitumen emulsion

3.2.1 Materials

3.2.1.1 Bitumen

Bitumen was obtained from Ceylon Petroleum Corporation. Since bitumen of penetration grade 80/100 is mostly used for manufacturing of bitumen emulsion in Sri Lanka, it was selected for the present study. A sample was analyzed under the method stated in ASTM D244 and the measured value was found to be 81 (1/10th of mm).

3.2.1.2 Acid

Hydrochloric acid was obtained from Nimbus International with the concentration of 35% w/w. Concentration was measured by acid-base titration with Sodium Hydroxide.

3.2.1.3 Chitosan

Water soluble Chitosan was obtained from Zhengzhou Sigma Chemicals Co.Ltd in powder form and it was dissolved in water to prepare a solution. Its specifications are given in Appendix A.

3.2.1.4 Water

Water (with drinking quality standard) was obtained from National Water Supply and Drainage Board, Sri Lanka. Water quality standard is given in Appendix B.

3.2.1.5 Kerosene

Kerosene which was used as the solvent was supplied by Ceylon Petroleum Corporation (CPC) with the Ceypetco product specifications (Appendix C) (“Specification for Lanka Industrial Kerosene P-012”, 2013)

3.2.1.6 Emulsifier

Two different emulsifiers were used along with Chitosan depending on what type of emulsion is produced. For CRS type emulsions, emulsifier N100L (Kao Corporations, Thailand) was used. It has a proven capability of producing CRS emulsions with aggregates used for roads construction in Sri Lanka.

For the production of CSS type emulsions Stabiram MS3 emulsifier was used. It was supplied by Nayler Chemical Co.Ltd, UK. This emulsifier has also been successfully used to produce CSS emulsions in Sri Lanka for years.

3.2.1.7 Stabilizer

Calcium Chloride was used as the stabilizer which was supplied by Weifang Orenyuan Chemical Co.Ltd with the purity of 74.2%. Purity was measured by the precipitation method. Known weight of Calcium Chloride is mixed with a known volume of water and Calcium Chloride solution was prepared. This solution was mixed together with a Sodium Carbonate solution of known strength. Resultant precipitant, Calcium Carbonate, was measured for its weight after placing it in a desiccator for 24 hours. Using this weight, purity of Calcium Chloride was calculated.

3.2.2 Equipment

Emulsification was done in a laboratory level colloid mill specially designed for the production of bitumen emulsion samples. It was manufactured by DenimoTech Company, Sweden. This machine has a production capacity of 300 l/hr and operates batchwise. A photograph of the mill is given in Figure 3.1.

Figure 3.1: Laboratory Mill for emulsion manufacturing

Source: Maga Neguma Emulsion Production Company (Pvt) Ltd

Machine consists of two separate tanks for the two phases; bitumen phase and water phase. In addition it has two pumps to feed those two phases at the desired flow rates into the mill. Bitumen pump has a fixed output rate of flow while water pump output flow rate can be varied.

Mill unit is the main component of the plant. It is a colloid mill which is adjustable for the gap between the stator and rotor. It has a variable rotational speed controller which can adjust revolutions per minutes (rpm) from 0 to 12000. Mill gap is set as 2.5 mm.

Temperature controllers are present to maintain the temperatures of liquids and flow lines. Indicators for temperature and rpm values are fitted in the control panel.

3.2.3 Preparation of Bitumen Phase

Bitumen phase consists of bitumen and kerosene. Bitumen was heated to temperature of 140-145°C by placing on a pot and applying fire (Figure 3.2). It was poured to the bitumen phase tank of the laboratory mill after reaching the required temperature range. As soon as it was poured, a measured volume of kerosene was added to the same tank and circulated inside the tank to mix properly.

Figure 3.2: Bitumen Heating

3.2.4 Preparation of Soap Phase

Soap phase consists of water, emulsifier, Chitosan solution, calcium chloride and hydro chloric acid. Measured volumes of all these ingredients except hydro chloric acid were put into a container based on selected recipes and were thoroughly mixed together using a stirrer (Figure. 3.3). pH value of the solution was measured and acid was added to bring the pH to the expected level. After preparation in external container soap solution was poured to the soap phase tank and was circulated inside the tank before sending to the production.

Figure 3.3: Soap Solution Preparation

3.2.5 Emulsion Production

Since the bitumen pump flow rate was kept constant, soap phase pump flow rate was adjusted to set the correct bitumen percentage in the emulsion in continuous operation. Soap phase flow rate was controlled by controlling rpm value of the pump. Through initial trials it was confirmed that for 63% bitumen percentage water pump rpm value should be at 1020 and for 64% it should be at 960. Before feeding to the mill both liquids were circulated initially inside their tanks and when rpm values became steady soap phase was first fed to the mill. Thereafter mill rpm was set to the machine at specified value of 9000 rpm. It is important to feed the soap phase first at the beginning as bitumen phase may cause the mill bound since bitumen viscosity is very high. Recipes of CRS1 and CSS1 emulsions are given in Tables 3.1 and 3.2, respectively.

When mill rpm value was set to 9000 bitumen phase was fed to the mill. First part of the mill output was not collected for testing as two phases might not be mixed properly. Sample collection point was indicated when the color of output emulsion was turned into brownish. After sufficient amount of sample was taken, feeding of bitumen phase was stopped but soap phase was continued to wash the mill. Each sample was produced sequentially following the above mentioned procedure.

Table 3.1: Formulation of CRS1 type emulsion

Ingredient	**Percentage of emulsifier replacement from Chitosan**					
	0%	**20%**	**40%**	**60%**	**80%**	**100%**
Bitumen (g)	4267	4267	4267	4267	4267	4267
Water (g)	2209.7	2209.7	2209.7	2209.7	2209.7	2209.7
Emulsifier (g)	15.3	12.2	9.1	6.0	3.1	0
Chitosan (g)	0	3.1	6.2	9.3	12.2	15.3
Calcium Chloride (g)	8	8	8	8	8	8
Kerosene (g)	167	167	167	167	167	167

Table 3.2: Formulation of CSS1 type emulsion

Ingredient	**Percentage of emulsifier replacement from Chitosan**						
	0%	**10%**	**20%**	**40%**	**60%**	**80%**	**100%**
Bitumen (g)	4200	4200	4200	4200	4200	4200	4200
Water (g)	2179	2179	2179	2179	2179	2179	2179
Emulsifier (g)	60	54	48	36	24	12	0
Chitosan (g)	0	6	12	24	36	48	60
Calcium Chloride (g)	8	8	8	8	8	8	8
Kerosene (g)	220	220	220	220	220	220	220

3.2.6 Sample Storing

Samples were stored in cans with closed lids preventing any material to be contaminated even air. It was kept at room temperature which was in the range of 26-30°C and sunlight was not allowed to fall into the container. Samples were taken out only for testing purposes.

3.2.7 Sample testing

All the samples were tested for the properties of Viscosity, Storage Stability, Settlement test and Sieve test as per the ASTM standard given under D244 (ASTM, 2009) while a visual inspection method was used for the break time test.

3.2.7.1 Viscosity

Viscosity of emulsion samples was measured using a calibrated saybolt furol viscometer with an orifice size of the furol tip is 3.17 mm which is complying with the specifications given (3.13 mm-3.17 mm) under ASTM standard (Figure 3.4).

Figure 3.4: Saybolt Viscometer to measure emulsion viscosity

3.2.7.2 Storage Stability and Settlement test

Both of these tests were done in similar way and only the storage time was different. Storage was done in a beaker closed to prevent air contamination as open storage causes the formation of a skin on top surface. Sample volume of 50ml from top and bottom were drawn out carefully using a pipette. Care was taken not to allow emulsion in the middle part of the beaker to flow in with top part. Drawn samples were kept in an oven at 163°C for 3 hours to measure the residue content. Percentage difference between the residue contents in top and bottom parts was taken as the measurement for both of these tests. The oven was calibrated to perform accurately at operating temperature.

3.2.7.3 Testing for breaking and setting behavior

Break and set time is the time that emulsion takes to revert into bitumen. After reversion, bitumen acts as the binder and adheres to the aggregate which increases the stiffness in the emulsion-aggregate mixture. This causes difficulty in further mixing of emulsion with aggregate. Depending on that time, emulsion application is determined. For the applications like cold mixing, higher pre mixing time is required and hence breaking and setting time needs to be high. Due to this reason slow setting type emulsions are used. Meanwhile surface applications require a faster breaking and setting time to open the road for traffic without delay. Therefore it is important to observe the effect on break and set time of emulsion after Chitosan is used as an emulsifier.

Break and set time was measured as the time taken to turn brown colored emulsion in to blackish when applied on an aggregate surface. This is a comparative study as it only suggests relative break and set time of emulsion with and without using Chitosan as an emulsifier.

Break and set time for CSS1 type emulsion was measured for two samples; one without Chitosan and the other with Chitosan replacement of 10%. In order to find the break and set time, industrial application called “cold mixing” of bitumen emulsion was used. Cold mix samples with generally accepted formulation given in Table 3.3 were prepared. The break and set time of emulsion was measured as the time for color change in the cold mix sample.

Both samples were prepared using similar aggregates to nullify any effect depending on the nature of aggregate on set time and the experiments were duplicated.

Required weights of aggregate were measured in each grade and they were well mixed using a spatula. Then water was poured onto the dry aggregate and the mixture was well mixed again. Next, emulsion was poured onto the wet aggregate mix and mixing was continued. Time taken for the color change of the bitumen emulsion from brown to black or blackish brown was observed and recorded.

Table 3.3: Formulation of Cold Mix design sample (500g of aggregate sample)

Component	**Weight (g)**
Aggregate	
*19mm	120
*12mm	280
* 600µm	100
CSS1 emulsion	40
Water	14

3.2.7.4 Sieve Test

Sieve test under ASTM D6933 covers to which extent the bitumen emulsion may contain particles which doesn’t pass through 850µm mesh.

3.3 Experimenting Chitosan as an additive to bitumen emulsion

Purpose of the second part was to test the outcomes when Chitosan was used as an additive for bitumen emulsion. There were two options of using as an additive; for CSS1 emulsion and for CRS1 emulsion. Based on the results of the first part of this research work it was identified that Chitosan has significantly altered the rheological properties of the emulsion. For CRS1 emulsion viscosity is the most critical property since it used as a surface application. In surface applications, maintaining the proper viscosity is important for both spraying and to prevent emulsion run off. However, for CSS1 type emulsion, viscosity is not the most significant property but maintaining of sufficient breaking and setting time is the major concern. Therefore Chitosan was only used as an additive to modify the rheology of CRS1 emulsion.

3.3.1 Bitumen Emulsion

ASTM complying CRS1 type of bitumen emulsion was used for modification with Chitosan. It was supplied by the Maga Neguma Emulsion Production Company (Pvt) Ltd. The initial properties of the emulsion before treated with Chitosan (i.e. 0% Chitosan) are given in 1st column of the Table 4.3.

3.3.2 Chitosan

Powdered Chitosan, specifications of which are given in appendix A, was used without any dissolving in water or any other medium.

3.3.3 Equipment

Hand mixture (Figure.3.5) was used to properly mix the emulsion and Chitosan powder together. This hand mixture has twin spindles and their rotational speed could be changed. It can be rotated at a maximum rotational speed of 1800 rpm and has 5 different variable speeds; 1800, 1525, 1250, 975 and 700 rpm. Spindles were dipped in emulsion contained in a beaker. The relative sizes of beaker and spindles are given in the Figure 3.5.

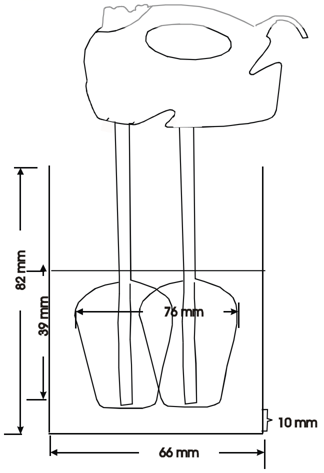


Figure 3.5: Sketch of mixing arrangement

3.3.4 Methodology

Six hundred grams (600 g) of bitumen emulsion was weighed to the beaker and spindles of the hand mixer were placed at the center of the beaker to provide a concentric position during mixing. Mixer was switched on and a stopwatch was used to record the mixing time. Then the

Chitosan powder was added to the center of the beaker which is also the midpoint between spindles. Mixing was continued for 5 minutes and at the end of that period, mixer was switched off and sample was taken out.

3.3.5 Sample Storage

Similar procedure was followed as explained in the section 3.2.6.

3.3.6 Sample testing

Similar procedure was followed as explained in the section 3.2.7.

4.0 Results and Discussion

4.1 Chitosan as an emulsifier

4.1.1 Compatibility for Cationic Slow Setting 1 type of emulsion

Production of CSS1 emulsions was only possible up to 20% (w/w) replacement of Chitosan as for replacements above that has caused mill bound without running. Such outcome may happen when mill could not handle higher viscosities than specified. Even at 20% replacement, viscosity was more than the acceptable level (20-100 Seconds) according to the ASTM standard. The resultant viscosities with addition of Chitosan are shown in Table 4.1. Viscosity was observed to be increasing exponentially at 20% replacement. Consequently, it was difficult to form an emulsion, instead clots were formed and the mill rotational speed which was set to 9000 rpm had dropped sharply during the feed time. The possible mechanism for this increasing behavior of the viscosity in the presence of Chitosan is explained in section 4.1.4.

4.1.2 Compatibility for Cationic Rapid Setting 1(CRS 1) type of emulsion

For CRS 1 type emulsion the maximum possible replacement of Chitosan was found to be 60%. A sharp drop of RPM was observed for the replacement of Chitosan above 60%. Further the sample produced with 80% replacement showed formation of clots and emulsion nature was lost showing similar behavior as in the case of 20% replacement for CSS1 type emulsion.

4.1.3 Optimization of properties

CSS1 and CRS1 emulsion samples were tested to find the variations observed with the increase of Chitosan replacement for the properties of viscosity, bitumen content, sieve test, storage stability, 5 day settlement and breaking time. Test results for CSS1 and CRS1 types of emulsion are given in Table 4.1 and 4.2, respectively. Since the viscosity has exponentially reached high values for 80% Chitosan replacement of CRS1 emulsions and 20% Chitosan replacement of CSS1 emulsion, testing for other properties was not practicable at mixing beyond those ratios.

Table 4.1: Properties of CSS1 emulsion

Property	**Replacement of emulsifier (%)**		
	0	**10**	**20**
Saybolt Viscosity (Seconds)	20	72	243
Bitumen Content (%)	62.8	63.1	63.0
Sieve test (%)	0	0	N/A
Storage Stability (24hr) (%)	-1.4	-0.4	N/A
5-day Settlement (%)	-0.6	0.2	N/A
Breaking time (minutes)	21	15	N/A

N/A – Not Applicable

Table 4.2: Properties of CRS1 emulsion

Property	**Replacement of emulsifier (%)**				
	0	**20**	**40**	**60**	**80**
Saybolt Viscosity (Seconds)	16	28	50	43	248
Bitumen Content (%)	63.8	63.5	63.8	63.3	63.5
Sieve test (%)	0	0	0	0	N/A
Storage Stability (24hr) (%)	-0.2	0.4	0	-0.8	N/A
5-day Settlement (%)	-0.6	0.8	1.6	1	N/A
Breaking time (minutes)	Instant	instant	instant	Instant	N/A

N/A – Not Applicable

4.1.3.1 Emulsion Viscosity

For CRS1 type of emulsions the most important rheological property is the viscosity since it is mainly used for surface applications such as sand sealing and chip sealing. With low viscosity the emulsion will run off without coating on the aggregates and with high viscosity it clogs the spraying nozzles thus preventing the uniformity of spraying.

Partial replacement of Chitosan has improved the viscosity of the emulsion significantly with compared to emulsion prepared without Chitosan. Figure 4.1 shows that viscosity which increases as the Chitosan replacement was increased. At 80% of Chitosan replacement, viscosity attained an extremely higher value of 248 seconds. This observation is very similar to CSS1 with 20% replacement (Figure 4.2). In both cases viscosity started to increase exponentially above a critical Chitosan to bitumen ratio as explained in section 4.1.4.

Controlled increase of viscosity is favorable for the emulsion application but too much increase would make it difficult for even spreading of emulsion and also cause handling difficulties. Depending on the type of crude oil, composition of bitumen varies. As explained in section 2.1.3.1, asphaltene content in the bitumen is responsible for the viscosity of bitumen emulsion. Bitumen emulsion manufacturers sometimes find it difficult to control the viscosity due to the variations in bitumen composition. In such situations, controlled increase in viscosity as observed with the Chitosan replacement would be favorable to maintain the properties within desired level.

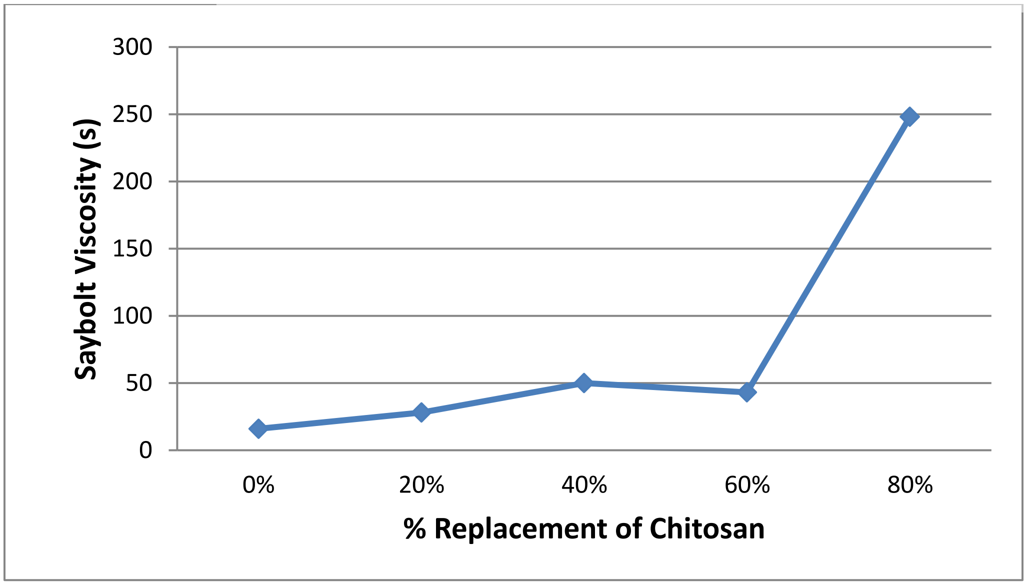


Figure 4.1 Viscosity of CRS1 type of emulsion

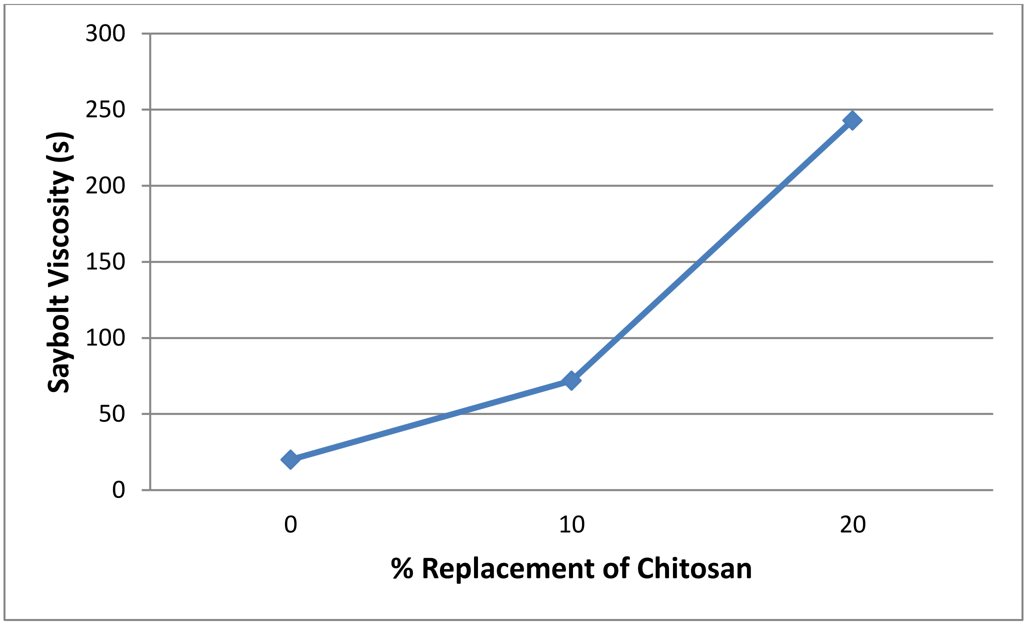


Figure 4.2 Viscosity of CSS1 type of emulsion

4.1.3.2 Storage Stability

Storage Stability is the deciding parameter for uniformity of dispersion of bitumen droplets in aqueous medium during the storage for 24 hours. If more particles are concentrated in top layer of emulsion during storage, it is called as "creaming" and concentration at bottom is called as "settlement".

Method of finding the storage stability is explained in section 3.2.7.2. Value of storage stability is obtained as the difference of Bitumen content at bottom layer and Bitumen content at top layer. The ASTM specified level of storage stability is ±1%. Emulsion tends to settle when storage stability is close to +1 and the emulsion tends to cream where it is close to -1.

Out of all Chitosan replacements for CRS1 type of emulsion, storage stability showed the highest potential for settlement with a value of 0.4 at 20% replacement and the best value of 0 at 40% replacement (Figure 4.3). At 60% it showed a high possibility of creaming. However all the values up to 60% replacement were within the ASTM specified level of ±1%. This result indicates the ability of bitumen emulsions produced with Chitosan replacement to retain uniformity during the storage.

Similar observation (Table 4.2) was made with CSS1 emulsion samples. Emulsion with 10% replacement of Chitosan showed storage stability of 0.2% which was well within the ASTM specified level of ±1%. Therefore it can be concluded that Chitosan replacement did not significantly affect the storage stability for 24 hours.

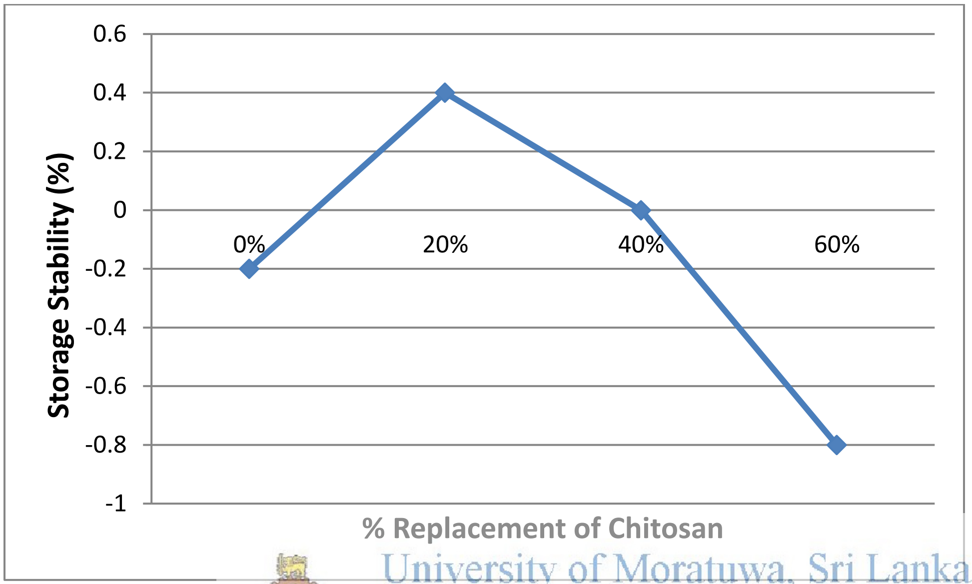


Figure 4.3: Storage Stability (24 hours) for CRS1 emulsion

4.1.3.3 Settlement Test

Settlement test is done to measure the long term stability of emulsion. When the emulsion is stored for long period of time without agitation it tends to either settle or cream. Generally accepted agitation cycle is “once in every two weeks”. If the emulsion is creaming or settling before that time it indicates an unstable emulsion. Settlement test can be performed at different storage times but, most standards have defined it for the settlement within 5 days. According to American Association of State and Highway Transportation Officials (AASHTO T59-08), the standard level of 5 day settlement is ±5%.

Five day settlement for CRS1 type emulsion has shown a maximum settlement tendency at the 40% replacement but all of those values were within the acceptable level for industry. Figure 4.4 indicates that the tendency of bitumen globules to settle increases with the increasing percentage of Chitosan replacement. All the samples produced with Chitosan replacement had positive values thus showing the settling tendency.

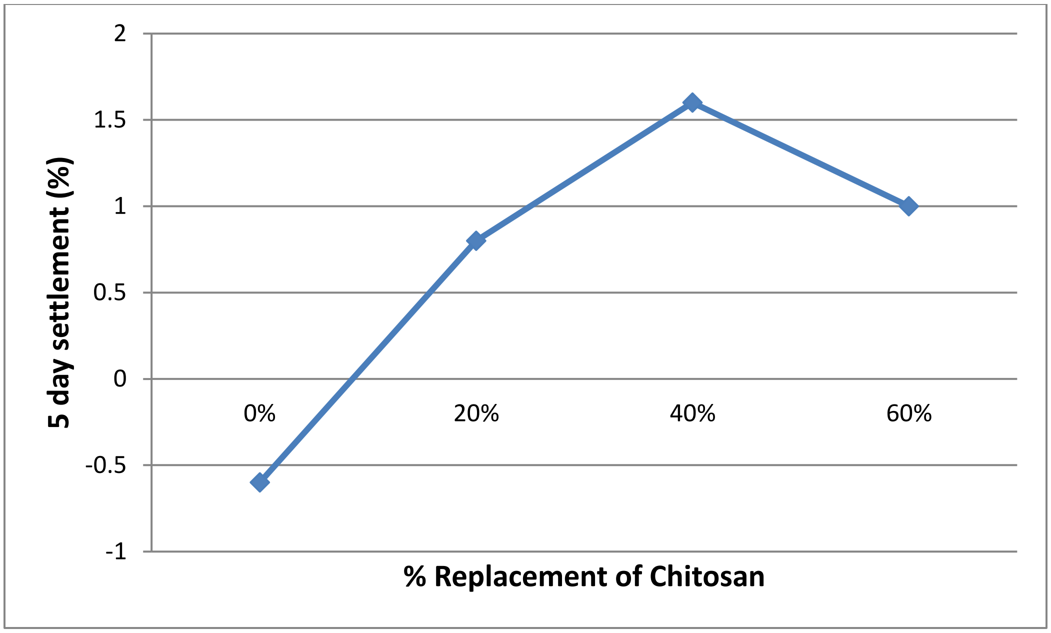


Figure 4.4: Settlement (5 day) of the CRS1 type of emulsion

Comparison of 5 day settlement with 1 day storage stability for CRS1 emulsions indicates that Chitosan replacement has a significant effect on settling tendency with storage time. In contrast the sample without replacement has shown negative or creaming tendency with the storage time. This behavior is indicated in Figure 4.5 in which the deference between the 5 days and 1 day (24hrs) for deferent percentages of Chitosan replacement was plotted. A similar tendency was observed for CSS1 type of emulsion also.

When Chitosan is added, interactions with multiple bitumen droplets increases. As a result, bitumen droplets coagulate and become large in size and weight, thus tend to settle with time. Hence replacement of conventional emulsifier by Chitosan may be useful to reduce the creaming tendency under cold weather climates where creaming during storage is a big problem.

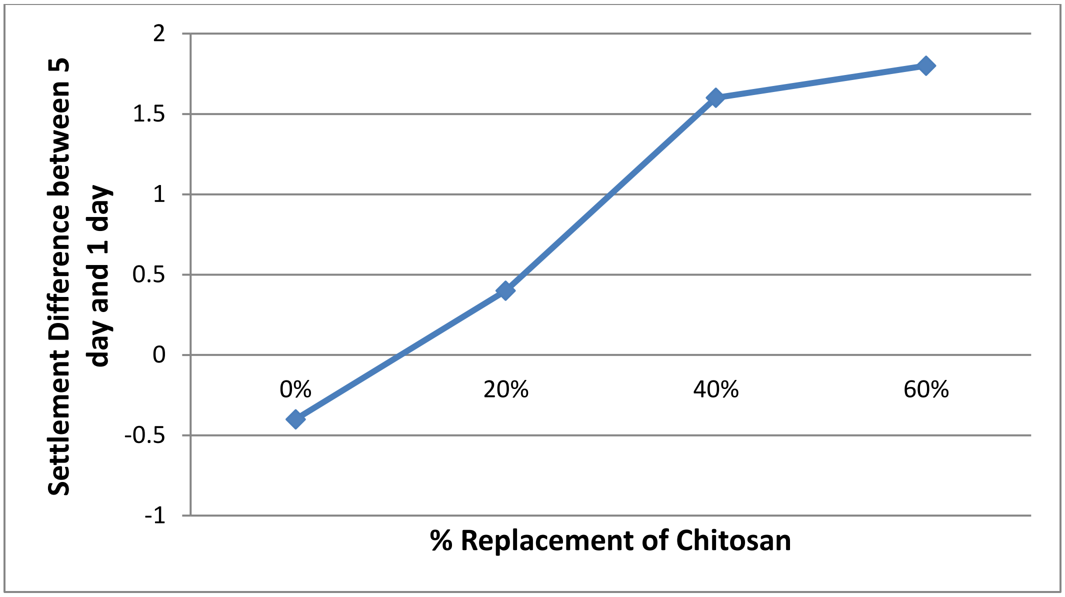


Figure 4.5: Settlement difference between 5 day and 1 day

4.1.3.4 Sieve Test

Sieve test reveals the presence of larger globules of bitumen that might not be found in the storage stability test. In the presence of such globules emulsion spraying does not provide uniform droplet distribution. Therefore, it is important to maintain the ASTM standard level of 0.1% of emulsion (ASTM D6933) weight or less retaining on the sieve. For both CSS1 and CRS1 type emulsions, Sieve test is at zero value in every sample up to 60% replacement. No clogs or globules were retained on the sieve. But with 80% replacement it was not possible for emulsion to pass through the sieve due to the high viscous or gelatinous nature.

4.1.4 Proposed model for explanation of results

When cationic surfactants are used as emulsifiers in bitumen emulsion process, they impart positive charge to the bitumen droplets to form positively charged colloidal particles. As per conventional description of emulsion, these positively charged colloidal particles repel each other and a stable emulsion is formed. This behavior is depicted in Figure 4.6.

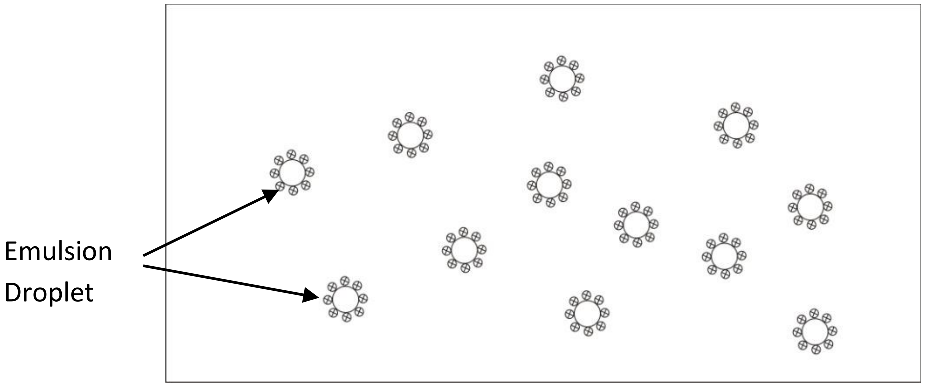


Figure 4.6: Colloid particles of bitumen emulsion being stable by repelling each other

When Chitosan is added, it attracts emulsion droplets as head groups (see section 2.1.3.3) of emulsifiers contain hydrogen which can form hydrogen bonds with oxygen atoms available in methylol, oxo and hydroxyl groups of Chitosan molecule (Figure 4.7). In addition to the hydrogen bonds, cationic charge available in the head group would create a stronger bond with Chitosan. At lower substitution of Chitosan, emulsion has more unbound particles than bound particles and eventually this turns to opposite as the Chitosan substitution increases.

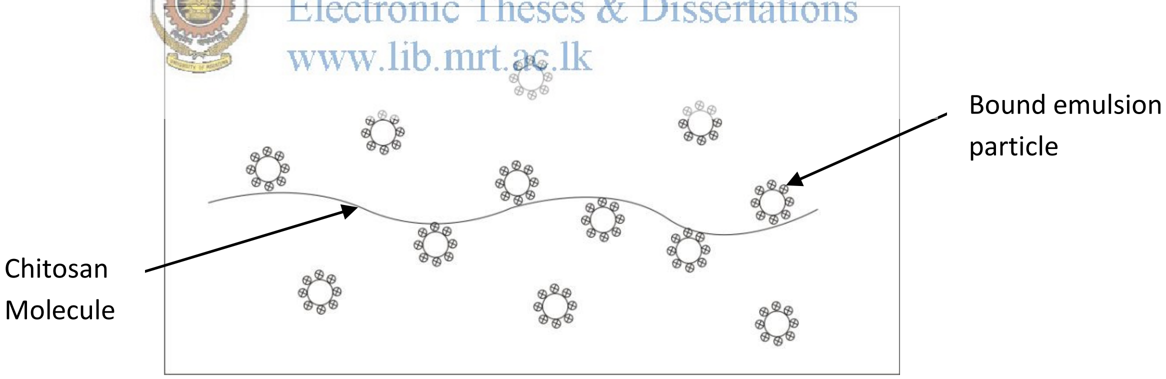


Figure 4.7: Bound particles and unbound particles

Chitosan molecule and emulsion particles bound to it are assumed to be moving as an individual colloid particle thus effectively forms a larger size particle or agglomerate with multiple cationic groups. It would also repel any unbound charged colloidal particles and similar large particles.

As the Chitosan percentage increases in the emulsifier it reaches the saturation limit where all the colloidal particles become bound (Figure 4.8). Emulsion viscosity assumed to be increased gradually up to this point.

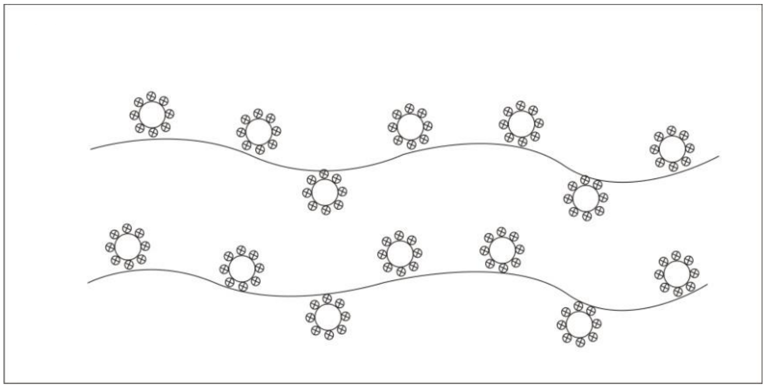


Figure 4.8: All particles bound to Chitosan molecules

Any substitution beyond that would create crosslinking between oppositely polarized groups of such agglomerates and eventually a network structure is formed. This network can be considered as an inter polymeric complex (Figure 4.9). As a result of the formation of these inter polymeric complexes liquid becomes a gel. This may result in exponential increase in viscosity at the inception of gelation as in the cases of 20% and 80% replacement of Chitosan in CSS1 emulsion and CRS1 emulsion respectively.

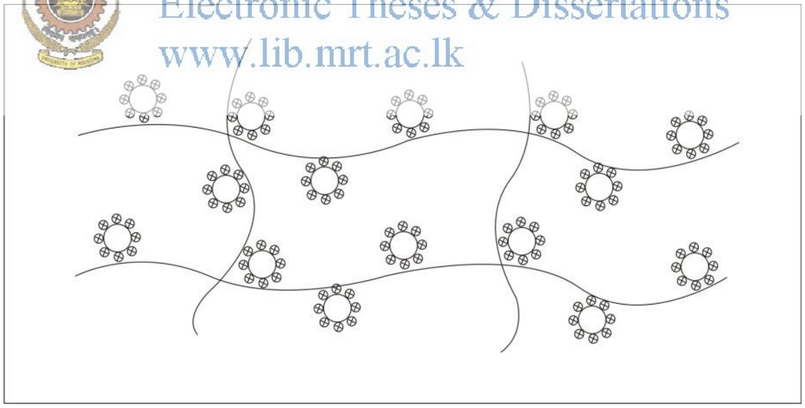


Figure 4.9: Interpolymeric Complex

Chitosan to bitumen ratio in 80% replacement of CRS1 and 20% replacement of CSS1 are 0.00288 (g/g) and 0.00286 (g/g) respectively (see appendix C). This result suggests that the exponential growth of viscosity started at the same Chitosan: Bitumen ratio in both emulsion types. Physical meaning of Chitosan: Bitumen ratio is the “number of bitumen particles being attached to a Chitosan molecule”. As explained by the proposed model, with the increase of

Chitosan replacement, Chitosan: Bitumen ratio increases. At a maximum Chitosan: Bitumen ratio, the emulsion becomes a gel and the viscosity increases exponentially.

4.1.5 Breaking and setting of Emulsion

Cold mix sample prepared using CSS1 type emulsion with Chitosan substituted emulsifier has turned black after 15 minutes while sample prepared without Chitosan took 21 minutes (Figure 4.10 and Figure.4.11). This implies that Chitosan substitution has accelerated the emulsion setting process. It may be due to the increase in electrostatic attraction to aggregate and also the increased chemical bond between bitumen and aggregate. A descriptive explanation is given in the next sections using theories given under sections 2.1.5.1-2.1.5.4.

Breaking and setting of CRS1 type emulsions occurred as soon as they were mix with aggregate as indicated by the formation of lumps with sand. Consequently the difference between emulsions, with Chitosan replacement and without Chitosan replacement could not be identified (Figure 4.12).

Figure 4.10: (a) CSS1 Emulsion produced with 10% of emulsifier replaced with Chitosan when applied on aggregate (Brown in color) (b) Emulsion color has turned in to black after 15 minutes

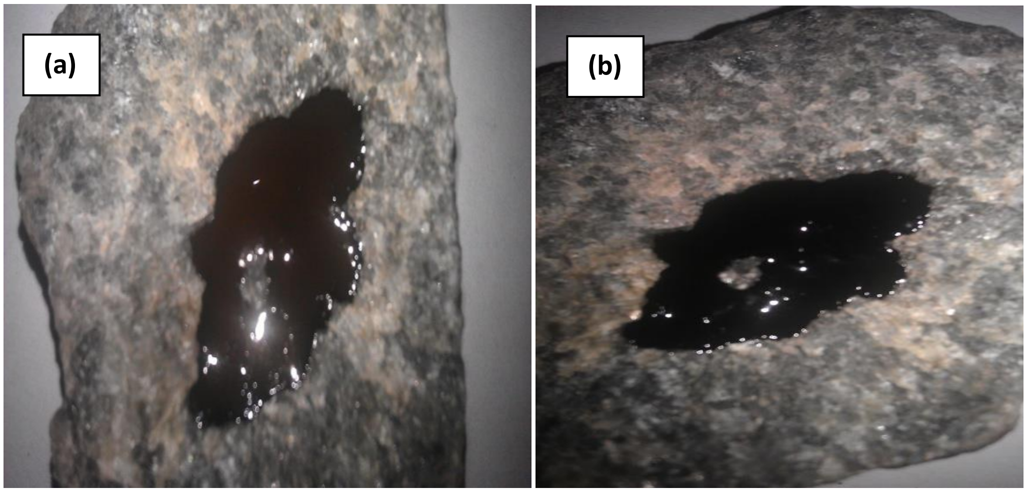


Figure 4.11: (a) CSS1 Emulsion produced without using Chitosan when applied on aggregate (Brown in color) (b) Emulsion color has turned in to black after 21 minutes

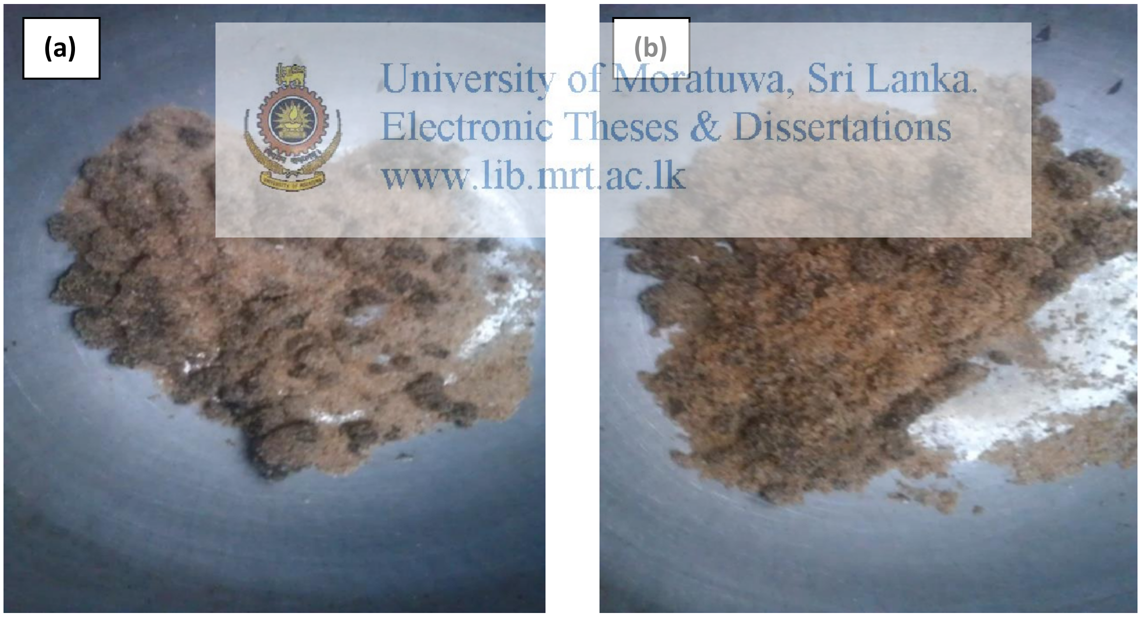


Figure 4.12: (a) CRS1 Emulsion produced with using Chitosan when applied on sand (b) CRS1 Emulsion produced without using Chitosan when applied on sand

4.1.5.1 Explanation using Electrostatic theory

Chitosan molecules are attached to multiple emulsion droplets. They have the ability of behaving as agglomerates which move separately and individually. Since both emulsion droplets and Chitosan molecules are positively charged, the net positive charge on agglomerates is greater than that of single emulsion droplet. As a result, the electronegativity difference between the aggregate and such agglomerate is higher than that of single emulsion droplet. Therefore in the presence of Chitosan the electrostatic forces between the agglomerates and emulsion become strong and eventually faster breaking and setting was observed.

4.1.5.2 Explanation using Chemical Bonding Theory

Cationic bitumen emulsion model suggests bitumen droplets being surrounded by cationic emulsifiers which are ionic. With the ionic charge present in the emulsion it reacts with the active sites of aggregate. These active sites are formed due to the fracturing of bonds between neighbor atoms as the aggregate is crushed.

These active sites of siliceous aggregate contain silanol groups which are weak acids. Cationically charged amine group of emulsifier is capable of forming a chemical bond between the amine and silanol group. When Chitosan added emulsion is present, it increases the amount of charged groups in the emulsion which have the tendency of forming such chemical bonds. Proton available in the silanol group can be attracted to the paired electrons in amine group of Chitosan molecule and it further increases the reaction rate. This results in faster breaking and setting time in the presence of Chitosan.

4.1.5.3 Explanation using Mechanical Theory

Mechanical theory is based on adhesion. Presence of Chitosan increases the surface area of bitumen droplets by forming agglomerates. Consequently adhesion between aggregates and emulsion enhances resulting in faster breaking and setting.

4.1.5.4 Explanation using Thermodynamic Theory

As explained in above theories Chitosan addition increases the net charge of emulsion. The increase in charge incorporates with rise in potential energy level of emulsion. Thermodynamic theory suggests that adhesive will interact with substrate to achieve the intimate contact by the establishment of intermolecular forces at the interface. This increase in potential energy would act as free energy and make the emulsion more reactive. Therefore it would try to minimize that free energy and come to a low energy state. This allows faster breaking since the driving force which is the potential energy difference is high.

4.2 Use of Chitosan as an additive to bitumen emulsion

These experiments were performed in a laboratory scale mixer. Since mixing was done using a spindle in an open vessel air trapping could be observed with rotating speeds above 700rpm. In contrast pilot scale mixing was done in a closed vessel and hence rotational speeds up to 9000rpm could be used without the problem of air trapping. Figure 4.13 shows the trapping of air bubbles at the top of the emulsion sample when rotational speeds above 700rpm were used in laboratory scale mixer.

Results for the properties of Viscosity, Bitumen Content, Storage Stability and Stability after 2 months are given in Table 4.3.

Table 4.3: Properties of CRS1 type emulsion with and without Chitosan

Property	Addition of Chitosan(w/w % of emulsion)				
	0%	**0.05%**	**0.10%**	**0.15%**	**0.20%**
Bitumen Content (%)	65.5	65.86	64.9	64.9	65.6
Saybolt Viscosity (Seconds)	26	38	44	61	92
Storage Stability (%)	0.2	-2.3	-1.8	1	1.6
Storage Stability after 2 months (Observation)	Settled	Settled	Settled	Settled	Settled

Figure 4.13: Air bubbles trapped at the top of the emulsion sample

4.2.1 Variation of Viscosity

Bitumen emulsion samples were prepared using Chitosan as an additive to the generally used formula which is given in Table 3.1. When the Chitosan percentage was gradually increased up to 0.2% (w/w) viscosity of the emulsion was observed to increase as depicted in Figure 4.14. When the Chitosan percentage was increased to 0.25% (w/w) the mixer spindle was slowed down and the emulsion was behaving like a gel. This situation was very similar to the 80% replacement of Chitosan in CRS1 in section 4.1.3.1. Therefore similar explanation given on the exponential increase of viscosity (in section 4.1.4) is applicable for explaining this situation too.

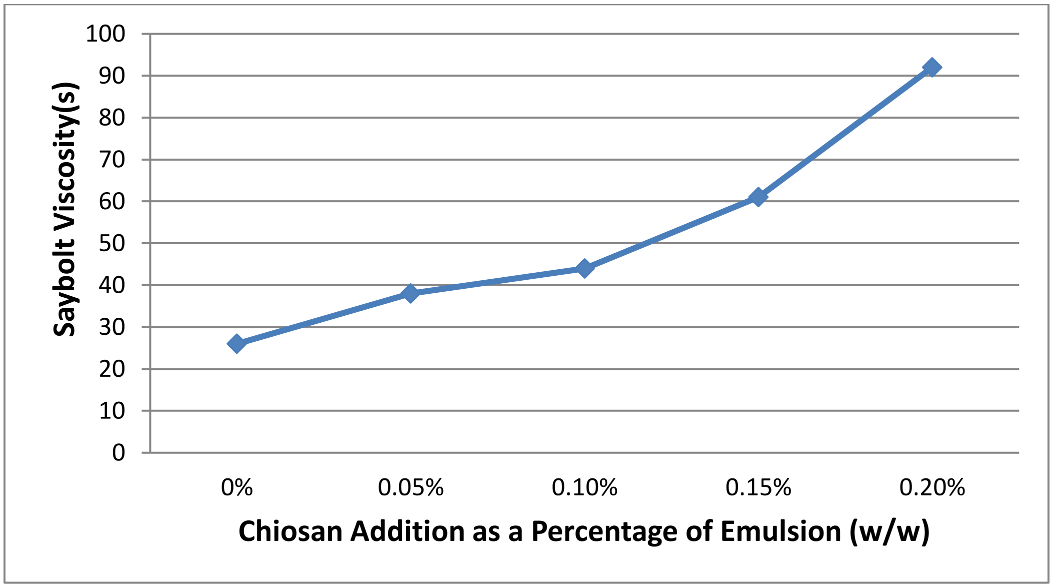


Figure 4.14: Viscosity of Chitosan modified emulsion

4.2.2 Storage Stability

Storage Stability is a measure of particle distribution in the emulsion. When Chitosan used as an additive to the emulsion storage, stability showed positive values below 0.1% and negative values above 0.1% (Figure 4.15). As explained in the section 4.1.3.2, positive value of storage stability means settling and negative value means creaming. Therefore this result indicates that initially Chitosan mixed emulsion is showing settling nature and when Chitosan addition increases it moves to the opposite direction and tend to float. All Storage Stability values were not complying with ASTM standard except for 0.15% addition. This can be overcome by increasing the stabilizer ($CaCl_2$) content which is used in the emulsification process. Stabilizers increase the density of the water phase and thereby reduce the settling of colloid particles.

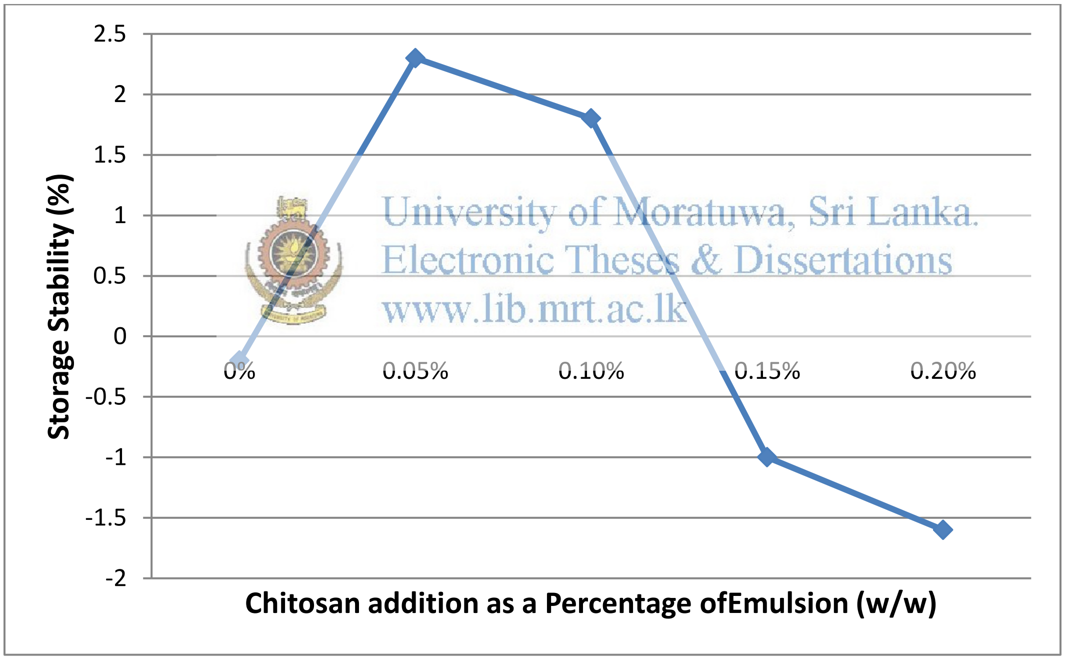


Figure 4.15: Storage Stability of Chitosan modified emulsion

4.2.3 Storage Stability in the long run

Emulsion samples with Chitosan (up to 0.2% w/w) and without Chitosan were stored in PET bottles and their long run stability was observed. After two months of storing, a phase separation was observed in emulsion sample with Chitosan. Figure 4.16(a) shows a separation of a clear supernant layer after 2 months in the PET bottles containing bitumen emulsion with Chitosan as an additive. No phase separation was observed for emulsion without Chitosan but sludge was formed at the bottom of the bottle due to the coagulation of colloidal particles. This sludge could not be dissolved even with shaking or agitation. This implies that emulsions without Chitosan has destabilized irreversibly. On the other hand emulsion with Chitosan mixed perfectly and supernant layer disappeared when the bottle was shaken even after two months (Figure 4.16(b)). This implies that these emulsions temporary or reversibly destabilize with storage.

When Chitosan is mixed with emulsion it forms agglomerates as explained in the section 4.1.4. Those agglomerates tend to settle in longer run due to their weight. Therefore separation occurs as the low dense water molecules retained at top. The separated larger particles remain in the bottom layer without coagulating in the presence of cationic groups. Chitosan prevents emulsion droplet from losing its positive charge and retains the stability for a longer time.

Since the formation of agglomerates is minimal in the emulsion without Chitosan no phase separation could be observed. Emulsion particles which lost their H+ ions due to reasons such as solubility of emulsifier, acidity of soap solution (pH), emulsifier concentration and phase-volume ratio would destabilize and form Van Der Waal forces with similar particles. Since they have lost their charge permanently such coagulated form cannot bring back to the emulsion form.

As per Sri Lankan Standards for bitumen emulsion (SLS 1405:2010) it is recommended to use bitumen emulsion within 45 days from production. Therefore storage in long run is important if any interruption caused by climatic conditions like heavy rain which might delay the application process. In such situations emulsion needs to store for a long period until conditions to apply the emulsion become favorable.

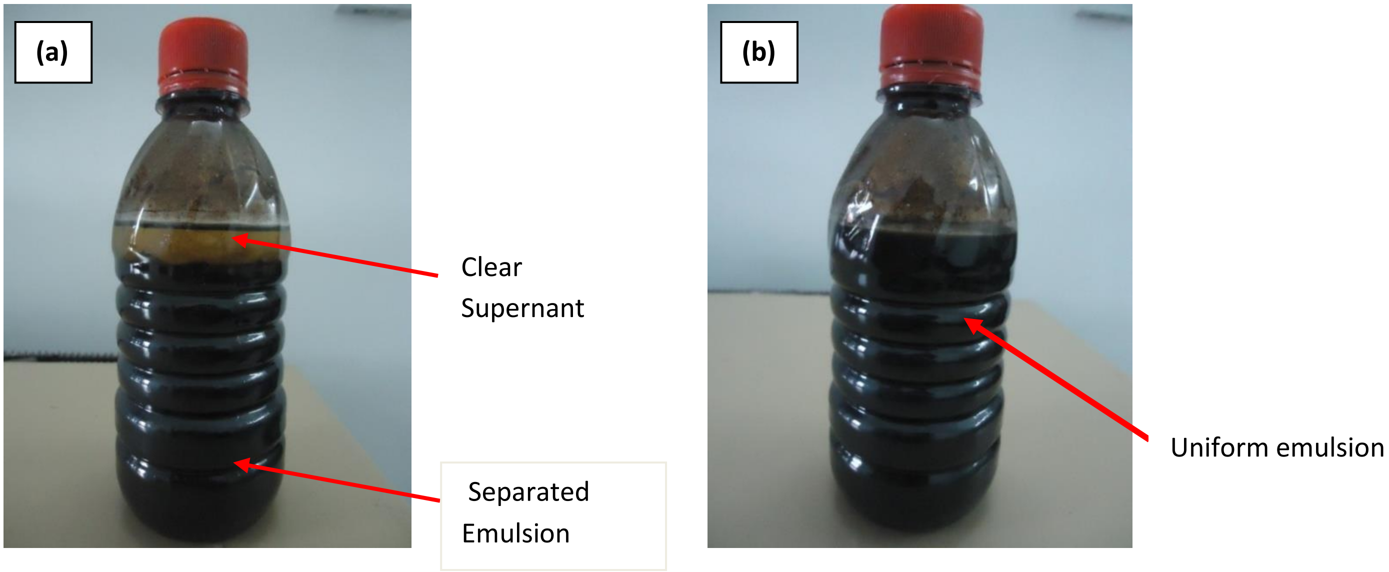


Figure 4.16: Long run storage stability (2 months) of bitumen emulsion with Chitosan as an additive (0.2% w/w) (a) Separation of layer (b) Homogeneous emulsion after mixing

5.0 Conclusion and future work

5.1 Conclusion

Chitosan was found to be suitable as a substitution for the currently using emulsifiers up to 60% replacement in CRS 1 type emulsions. Improvement to viscosity could be achieved up to 40-50 SSU as compared to 16 SSU in the original recipe. A stable emulsion could be formed without hindering the compliance to ASTM standard for storage stability (ASTM D977). Results of settling test indicated that Chitosan as an emulsifier increased the settling tendency of emulsion. However both storage stability and 5 day settlement values up to 60% replacement were within the acceptable level for the industry. Breaking and setting characteristics of CRS1 type emulsions with and without Chitosan replacement were almost the same and it can be concluded that Chitosan replacement had no significant effect on break and set time for CRS1 type emulsions.

For CSS 1 type emulsions, Chitosan as an emulsifier was successful at 10% and showed an improved viscosity of 70SSU as compared to 23SSU in original recipe. It showed a faster breaking emulsion when mixed with the aggregate thus Chitosan replacement has changed the break time of emulsion. Therefore it can be recommended to use Chitosan replacement up to 20% in cases where faster emulsion breaking is required or to use with less reactive aggregates which take longer break time.

In both CSS1 and CRS1 emulsions viscosity has exponentially increased after a saturation point of Chitosan substitution which reached approximately at Chitosan: Bitumen ratio of 0.028. After that point gelation effect was observed instead of an emulsion and a physiochemical model was developed to explain the observed results.

When Chitosan is added as an additive to CRS1 emulsions it showed that Chitosan acts as a viscosity modifier but it increased the settling tendency of emulsion. Results of Storage stability indicated that when Chitosan addition was increased emulsion tends to settle more. Thus it can be used to improve viscosity at the point of use when high viscosity is demanded. Since addition of Chitosan has not delayed the breaking, this can be used to improve viscosity without hindering the intended use. Destabilization of Chitosan added emulsion was temporary or reversible when stored for longer times up to two months. This is beneficial in cases where emulsion has to store for a long time.

5.2 Future Work

Chitosan used in this research is having a DD value of 95.5%. Emulsification capacity can be tested for different DD values as the cost of Chitosan is dependent upon the DD. Therefore optimizing the DD would give an economical output.

Water soluble Chitosan was used in these experiments but of acid soluble Chitosan is also available. Similar experiment can be done for acid soluble Chitosan as it may produce different results.

Chitosan replacements were done based on the specified dosage of an already using emulsifier. If Chitosan at 100% were used with different dosage without adding any other emulsifier that could give different results and even might be successful at full replacement. Therefore it is interesting to study the properties of bitumen emulsion when Chitosan is used as the only emulsifier with different dosages.

Mixing mechanism can have a significant impact over final solution properties. Mixing mechanism when Chitosan is used as an additive can be changed and the differences in each method can be found.

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Appendix A: Specifications of Chitosan

Item	Standard	Testing Result
Character	Straw Yellow Powder	Straw Yellow Powder
pH	3～6	5.3
Appearance of the Solution	Colorless Transparent	Colorless Transparent
DAC	≥90%	95.5%
Loss on Drying	≤10.0%	8.8%
Residue on Ignition	≤1.0%	0.78%
Viscosity	20-200 MPA.S	70MPA.S
Solubility	Over 99% in Water	Over 99.5% in Water

Appendix B: Drinking Water Standards

Source: Sri Lanka Standards for potable water – SLS 614, 1983

PARAMETER	Highest Desirable level	Maximum permissible level
A. Physico-Chemical		
Electrical conductivity at 25^{0}C µs/cm	750	3500
Total solids (mg/l)	500	2000
Colour (Hazen Units)	5	30
Taste	Unobjectionable	-
Odour	Unobjectionable	-
Turbidity (NTU)	2	8
Chloride (Cl^-) (mg/l)	200	1200
Fluoride (F^-) (mg/l)	-	1.5
Iron (Fe) (mg/l)	0.3	1
Manganese (Mn) (mg/l)	0.05	0.5
Copper (Cu) (mg. I)	0.05	1.5
Zinc (Zn) (mg/l)	5	15
Calcium (Ca) (mg/l)	100	240
Magnesium (Mg) (mg/l)	30	150
Total Phosphates (PO_4^{3-}) (mg/l)	-	2.0
Sulphate (SO_4^{2-}) (mg/l)	200	400
Total Alkalinity (as $CaC0_3$) (mg/l)	200	400
Total Hardness (as $CaC0_3$) (mg/l)	250	600
Free Ammonia (as NH_3) (mg/l)		0.06
Nitrate (NO_3^-) (mg/l)	-	45
Nitrite (NO_2^-) (mg/l)	-	0.01
pH	7.0 – 8.5	6.5 – 9.0
Arsenic (As) (mg/l)	-	0.05
Cadmium (Cd) (mg/l)	-	0.005
Chromium (Cr) (mg/l)	-	0.05
Cyanide (CN^-) (mg/l)	-	0.05
Lead (Pb) (mg/l)	-	0.05
Mercury (Hg) (mg/l)	-	0.001
Selenium (Se) (mg/l)	-	0.01
Free Residual Chlorine (as Chlorine) (mg/l)	-	0.2
Polynuclear aromatic hydrocarbons (mg/l)	-	0.0002
Phenolic compounds (as phenolic OH) (mg/l)	0.001	0.002
Grease & Oil (mg/l)	-	1.0
COD (Chemical Oxygen Demand) (mg/l)	-	10
Radioactive materials		
Gross alpha radioactivity (pC/I)	-	3
Gross beta radioactivity (pC/I)	-	30
B. Bacteriological		
Total Coliforms / 100 ml	Absent in (i) 95% of the samples in a year and (ii) in any two consecutive samples	10
E.Coli/100ml	Absent	Absent

Appendix C:

Calculation of Chitosan: Bitumen Ratio

CRS1 Emulsion

Bitumen percentage in emulsion as a fraction = 0.64

Emulsifier percentage as a fraction = 0.0023

Fraction of Chitosan replacement of emulsifier = 0.8

Therefore, Chitosan percentage as a fraction = 0.0023*0.8

= 0.00184

Chitosan: Bitumen Ratio = 0.00184:0.64

= 0.00288

CSS1 Emulsion

Bitumen percentage in emulsion as a fraction = 0.63

Emulsifier percentage as a fraction = 0.009

Fraction of Chitosan replacement of emulsifier = 0.2

Therefore, Chitosan percentage as a fraction = 0.009*0.2

= 0.0018

Chitosan: Bitumen Ratio = 0.0018:0.63

= 0.00286

Appendix D: Specifications for Industrial Kerosene (P-012) - Ceylon Petroleum Corporation

Property/Test	Test (IP)	Method(ASTM-D)	Specifications
Appearance			Clear, bright and visually free from solid matter undissolved water at normal ambient temperature
Colour, visual			Yellow
Density @ 15º C kg/m³	160	1298	775-840
DISTILLATION	123	86	
IBP º C			Report
10% Vol. @ º C			Maxc. 205
20% Vol. @ º C			Report
50% Vol. @ º C			Report
90% Vol. @ º C			Report
End Point º C			Max. 300
Residue % Vol.Max			1.5
Loss % Vol. Max.			1.5
COMBUSTION			
Smoke point mm		1322	19
Flash point °C	170	56	Min 38
COMPOSITION			
Acidity, total mg KOH/g	354	3242	0.05
Aromatic % Vol. Max.	156	1319	25.0
Olefin, % Vol. Max.	156	1319	5.0
Sulpher, total % mass Max.		4294	0.30
Sulpher, Mercaptantotal % mass Max.	342	3227	0.003
Or Doctor Test	30	4952	Negative
Cu Corrosion 2 hrs. @ 100 º C	154	130	1