DEVELOPMENT OF SILANE/SILOXANE EMULSIONS FOR APPLICATION IN BUILDING PROTECTION

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A thesis submitted for the degree of
Doctor of Philosophy

by

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January 1996

ACKNOWLEDGMENTS

I am indebted to many people for their assistance in the completion of this research work. While it is impossible to mention all the names, I wish to thank the following persons:

Dr. Douglas A. Kagi for his guidance, constant help and support during the course of this research;
Mr. Gary Holliday for his support and exchange of ideas;
Dr. Maurice Porter (Maurice R. Porter & Associates, England) for his advice on surfactants;
Dr. Andrew Smallridge for his assistance in matters relating to ^{29}Si NMR;
Prof. John Stearne for his encouragement and support;
Associate Prof. John Casey for his constant help;
Prof. Robert Snow (RMIT), who fostered my enthusiasm in many different ways;
The Technical Staff of the Department of Chemistry and Biology, especially **Mr. Vince Murone** for technical help, **Mr. Ian Sullivan** and **Ms. Min Nguyen** for providing useful help when desired;
Mr. Rod Flentje, Department of Civil Engineering for testing the compressive strength of concrete;
Mr. Anthony Caselli (Tech-Dry) and all my colleagues who have contributed to many valuable discussions.

Special thanks are due to:

My **Mother** for implanting in me the ambition and desire to pursue research work;
My wife, **Chau**. Without her inspiration, support and encouragement this thesis would never have been completed;

My children **Joanne** and **Nicholas** for their understanding and support during the course of this research.

The opportunity to undertake the research work at Victoria University of Technology under the Australian Postgraduate Research Award (Industry) provided by the Australian Government in conjunction with Tech-Dry Building Protection Systems Pty. Ltd. is gratefully acknowledged.

PREFACE

This project was an industrial research project sponsored by the Australian Government under the Australian Postgraduate Research Award (Industry) in conjunction with Tech-Dry Building Protection Systems Pty. Ltd as the industrial partner.

The project was aimed at developing silane/siloxane emulsions for concrete protection. The research area required multi-disciplinary input and the project was oriented towards academic and commercial research with a possible market outcome.

The academic and commercial aims of the project have been achieved. Part of the academic results of the project have been accepted for publication as a refereed paper:

a. "Novel Silane/Siloxane Emulsions for the Impregnation of Concrete" to be published in *Surface Coatings Australia*.

The commercial basis of the results has been lodged as patent applications:

b. "Method of Producing Stable Silane/Siloxane Emulsions for Rendering Masonry Surfaces Water Repellent", Australian Provisional Patent Application, *PM 2952*, 1993.

c. "Silane/Siloxane Emulsions For Masonry Surfaces", International Patent WO 95/16572.

ABSTRACT

Novel silane/siloxane emulsions for rendering concrete surfaces water repellent have been developed and patented. These novel emulsions were prepared from alkylalkoxysilanes as the base materials. One novel emulsion was composed of an alkylalkoxysilane and a neutralised polyisobutylsiloxane latex. The latex was prepared by the emulsion polymerisation of commercial isobutyltrimethoxysilane. The other novel emulsion was prepared by emulsification of a mixture of a silicone fluid and an alkylalkoxysilane in water with an amine soap as surfactant. A particular amine soap was chosen as a deactivatable surfactant to deliver very little negative beading effect at the surface of the substrate. The emulsions developed in this research contain no solvent. Therefore they comply with various regulations regarding volatile organic content (VOC). They are non-toxic and non-flammable, and may be considered as environmentally friendly materials.

The novel silane/siloxane emulsions were prepared as concentrates which can be transported and then diluted on site with water for application. They are stable and storable as concentrates over a long period of time. The emulsions are effectively neutral and maintain a high level of original alkylalkoxysilane on long term storage.

Experimental results indicated that the emulsions developed by the method of this research were very effective for concrete protection due to their high penetrating power, their stability to the alkaline environment and their ability to protect concrete from the intrusion of water and chloride ion. Their performance was comparable to solvent-based products in terms of stability, beading effect, penetration depth, water repellency, alkali resistance, UV resistance and the efflorescence resistance of the treated concrete.

The mechanism of the emulsion polymerisation process of isobutyltrimethoxysilane, the characteristics of the polyisobutylsiloxane latex and the properties of the novel silane/siloxane emulsions were studied in this research.

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CHAPTER ONE

Introduction

Concrete is one of the most versatile and durable construction materials. The high degree of durability of concrete under normal conditions of exposure has been shown by the vast number of structures in which concrete has been used successfully over the past 100 years or so. However, concrete is not immune to the action of many chemical substances entering from the surrounding environment. It has become evident that concrete, especially reinforced concrete is the subject to a number of mechanisms of deterioration. The corrosion of steel in concrete has received increasing attention in recent years because of its widespread occurrence in certain types of structures and the high cost of repairs.

Corrosion of reinforced steel in concrete is a complex process and the deterioration of steel-reinforced concrete is affected by various factors. The main factors responsible for the corrosion of steel reinforcement in concrete are chloride ion, and carbonation of the concrete due to carbon dioxide. These factors and the presence of moisture and oxygen, interrupt the passivating film due to alkalis on the embedded steel and this leads to corrosion.

The corrosion of reinforcing steel in concrete, either due to the ingress of chloride ions or the carbonation of the concrete is now widely known and both these mechanisms of deterioration involve moisture as a main factor. Water carries harmful substances into concrete. The presence of water in the concrete also lowers the electrical resistivity of the concrete which leads to corrosion of the reinforcing steel.[1,2,3,4] Water creates the electrolyte portion of the corrosion cell inside the concrete and supports electrochemical corrosion of the steel. It has been reported that the corrosion rate of embedded steel in concrete structures would be reduced if the moisture content in concrete is minimised, even when concrete is carbonated or contaminated with chloride ions.[5,6,7] Therefore, making the concrete water repellent is a practical way to protect the steel from corrosion because water is an essential element of deterioration and by excluding external water, the rate of the corrosion process may be greatly reduced.

Alkylalkoxysilanes have been shown to be very effective in the protection of structural concrete against corrosion of embedded steel,[8,9,10] and have been used for making masonry and other substrates water repellent for many years. Silanes were first proposed as impregnants for concrete in 1969 by Dynamit Nobel AG in West Germany. Since then, a large number of chemical companies in the world have attempted to develop their own materials for concrete protection, and silanes in various organic solvents such as alcohols, or hydrocarbons, have been in the market for many years. However, the solvents used to carry the active material to the concrete substrate are generally flammable and have become increasingly expensive. In addition, the odour, the environmental effects and the physiological effects of organic solvents are important factors against the use of organic solvents. With the advent of volatile organic compound (VOC) emission regulations, the use of organic solvents in silane and siloxane formulations must be limited or eliminated.

Water-based materials in the form of the alkali metal organosiliconates have been used for many years. These solutions are highly alkaline and are therefore difficult to handle and are corrosive. In addition, the alkali metal methylsiliconates are not suitable for the treatment of alkaline substrates containing free lime and having a pH of 8 or more.[11]

In recent years, various aqueous emulsion-type silicone compositions have been developed in Germany, the United States and Japan in an attempt to overcome the problems of solvent-based products and the alkalinity of organosiliconates. However, the performance of the commercially available emulsions and compositions is not comparable to organic solvent-based silane products in terms of stability, penetration depth, and the beading effect of the treated substrate. Therefore, it is continually desirable to provide alternative aqueous water repellent silane emulsions which are stable, capable of effectively impregnating alkaline substrates and achieving a desirable water repellent effect.

The object of this research project was to develop stable silane/siloxane emulsions for concrete protection which may be delivered to the substrate in water and where the penetration into the substrate is similar to that achieved with organic solvent-based materials. It was aimed at solving complex problems relating to the preparation, stability and the performance qualities of silane/siloxane emulsions.

The essential requirements for the development of silane/siloxane emulsions in this research were:

a) the selection of raw materials was limited to commercially available materials;

b) the technology would be industrially applicable;

c) the emulsions would have a long shelf life and the active alkylalkoxysilanes would not be hydrolysed in the emulsions during storage;

d) the emulsions could be prepared as concentrates which may be diluted with water to achieve a stable emulsion for low concentration application;

e) the performance of the novel emulsions in terms of beading effect, penetration depth, alkali stability, water absorption, chloride ion resistance and UV resistance of the treated substrates, would be comparable to organic solvent-based products containing the same concentration of alkylalkoxysilane.

CHAPTER TWO

Literature review

2.1. Silicon-based water repellents for the impregnation of concrete

Organo-silicone compounds such as siliconates, silanes, siloxanes and polysiloxanes have been used for the impregnation of mineral building materials for many years. Water repellent treatment of concrete with organo-silicone compounds has many advantages. Organo-silicone compounds are hydrophobic materials or materials which become hydrophobic on application to building substrates. They have the ability to impart concrete surfaces with water repellent properties and therefore prevent harmful salts dissolved in water entering the concrete structure. As the silicone treatment merely coats the walls of the capillaries and pores and does not seal the openings of the capillaries, there is no obstruction to the passage of water vapour. In general the impregnation causes no effect on appearance, therefore, it is practically impossible to distinguish a treated concrete surface from an untreated surface. Untreated surfaces darken on wetting with water which does not occur with water repellent surfaces. According to Wittmann,[12] the speed of calcification, particularly in fresh concrete, will be slightly increased by the use of water repellents. The impregnated concrete surfaces have less tendency to become dirty. This is due to the inactivation of capillary absorptivity and the dirt deposited on the treated surface is not washed into the capillary system of the concrete when it rains, but stays on the surface and is washed away. A further advantage of impregnated, prefabricated concrete components is evident if the concrete tends to form a network of hairline cracks. There is reduced absorbency in the region of the cracks as the dirt cannot accumulate there, thus preventing the area from becoming unsightly, even after a period of several years. Lime erosion on prefabricated concrete parts can be prevented by carrying out in-plant impregnation in good time. The impregnants may be re-applied after some years in certain circumstances and some form good primers for other types of coating.

Silicon compounds can be divided into three broad classes - monomers, oligomers and polymers - and they can be further classified according to the nature of the functional groups attached to the silicon atom. The hydrocarbon groups in silicon compounds are referred to as "organofunctional groups" while the hydrolysable groups such as chloro or alkoxy attached to the silicon atom are referred to as "silicon functional groups". The chloro or alkoxy functional groups provide a position on silicon to react with siliceous and similar substrates, while organofunctional groups provide hydrophobicity to the film lining the capillaries of the substrates.

The types of silicon materials currently available in the market can be classified into three categories. These are Q-structure materials (silicates) containing four silicon functional groups and no organofunctional groups, T-structure materials (siliconates, siloxanes and silanes) containing three silicon functional groups and one organofunctional group and D-structure materials (silicones or silicon resins) containing two silicon functional and two organofunctional groups (Figure 2.1). According to McGettigan,[13] it has been recognised in the silicone raw materials manufacturing industry that the compounds which have the potential to provide long term durability are those with T structures. Silanes and siloxanes have unequivocal advantages over other T, Q, or D-structure materials as silicone impregnants.

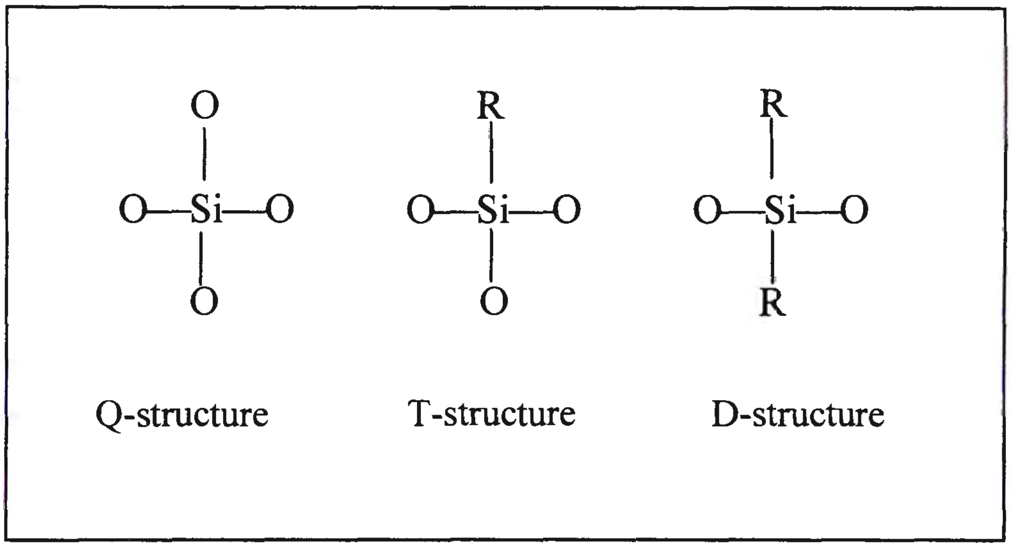


Figure 2.1. Nomenclature of the silicon compounds

2.1.1. The use of alkylalkoxysilanes for concrete protection

Alkylalkoxysilanes have become of more and more importance as impregnating agents for building protection and the effectiveness of silanes in retarding the corrosion of reinforcing steel in concrete has been widely recognised.[8,9,10] According to Weber,[14] the use of silanes for concrete protection has many advantages. Silanes have great penetrating power into substrates due to their small molecular size, and therefore they can provide long-term protection to reinforced concrete. The substrates to be treated with silanes do not need to be air dry and silanes improve the frost resistance and the freeze-thaw durability of the treated concrete in field exposure.[12,15]

The production of alkylalkoxysilanes is a two-step process,[16] starting from the hydrosilylation of α-olefins and trichlorosilane followed by esterification of the trichlorosilyl group as shown in Scheme 2.1.

$$\mathrm{Cl_3Si{-}H} \;+\; \mathrm{CH_2{=}CH{-}(CH_2)_{n-2}{-}CH_3}$$

$$\text{Pt catalyst}\;\Big\downarrow\;\text{Hydrosilylation}$$

$$\mathrm{Cl_3Si{-}(CH_2)_n{-}CH_3}$$

$$\text{+3 ROH}\;\Big\downarrow\;\text{Esterification}$$

$$\mathrm{(RO)_3Si{-}(CH_2)_n{-}CH_3} \;+\; 3\,\mathrm{HCl}$$

$$(\mathrm{R} = \mathrm{CH_3}, \mathrm{C_2H_5};\ 2 \le n \le 17)$$

Scheme 2.1. Technical synthesis of alkylalkoxysilanes

Alternative synthetic methods of producing alkylalkoxysilanes have been reported. They include the hydrosilylation of α-olefins with trialkoxysilanes,[17,18] the reaction of tetraalkoxysilanes with alkyl-Grignard compounds[19,20] or the so-called direct synthesis from the silicon element and alkyl chlorides[21] with subsequent esterification of the trichlorosilyl group.

The action of alkylalkoxysilanes in rendering concrete surfaces hydrophobic is based on the fact that when an alkylalkoxysilane is applied onto an alkaline surface, the atmospheric moisture, and in some cases the water that is present in capillaries or pores in the substrate, causes the alkoxy groups to be hydrolysed and alkylsilanols are formed as intermediates. The hydroxyl groups of the silanols react with the hydroxyl groups of the mineral substrate, and with other hydroxyl groups of silanols, forming siloxanes. A bond between the alkyl siloxane and the mineral boundary surface is produced, in which the alkyl group of the siloxane is exposed on the surface. This boundary surface bond greatly increases the surface tension of the mineral substrates to water, and the surface becomes water repellent (Figure 2.2).

The hydrophobic groups are chemically bonded to the concrete substrate and the water repellent property of the treated substrate can only be lost when either the bond of the hydrocarbon group and the silicone atom (R-Si), or the siloxane linkage (-O-Si-O-) between the silane/siloxane molecules and between the silicone and the substrate is destroyed. In the first case, a Si-C bond is extremely strong and in the second case, the only reagents which will break the Si-O bond belong to the same group of materials required to destroy the -Si-O-Si-O- bonds of the concrete itself.[22]

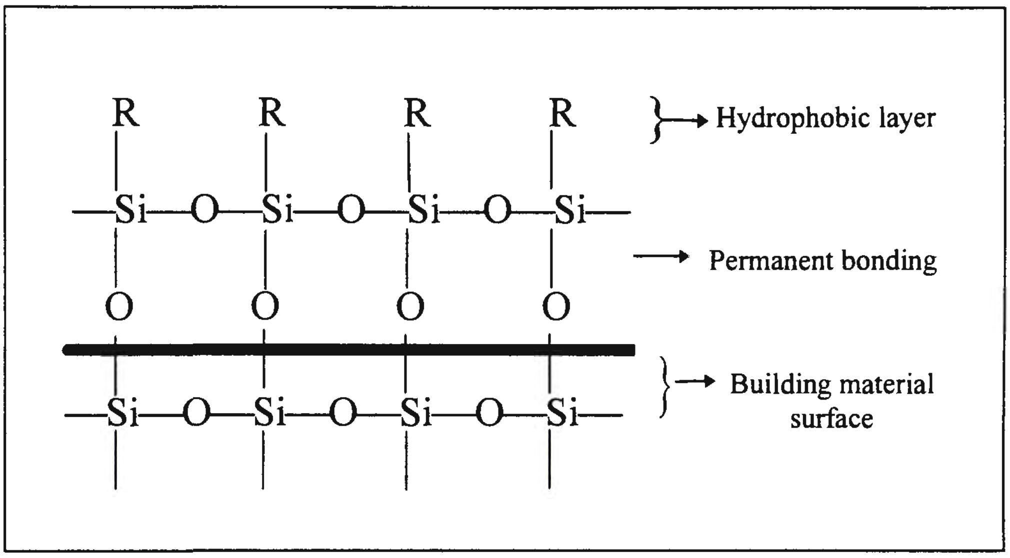


Figure 2.2. Reaction of alkylalkoxysilane and concrete substrate

2.1.2. Aqueous silane/siloxane water repellents

Solutions of silanes/siloxanes in various solvents such as alcohols, or hydrocarbons, have been used for treating masonry surfaces for many years. In general, with the correct choice of active material, these products have been technically successful in terms of good penetration depths, low water absorption of the treated substrate and alkali stability of the final polymer. However, the limitations of the organic solvent-based solutions are the toxicity and flammability of the solvent employed. Moreover, the expense and difficulty of the safe storage and transport of flammable and toxic solvents is also a factor against the use of solvent-based products. Therefore, there is now an increasing demand for water-based materials which may be delivered to the substrate in water, and which exhibit a performance which is similar to that achieved with solvent-based products.

There are a number of ways whereby organosilicone substances can be made aqueous where the active materials are dissolved or dispersed in water. Basically, these aqueous materials are siliconates, silanols, silicone emulsions, silicone microemulsions and silane/siloxane emulsions.

2.1.2.1. Siliconates

Alkali metal alkyl siliconates have played an important role as aqueous silicone masonry water repellents up to the present time. Highly alkaline alkali metal methylsiliconates such as potassium methylsiliconate [$CH_3Si(OH)_2\ O^-K^+$] have been used since the end of the 1940s. They are miscible with water in any desired proportion with indefinite storage stability. When applied onto building materials, siliconates react with atmospheric carbon dioxide to form water repellent polysiloxane polymers or di-siliconate salts and salts such as alkali carbonates. The main application of siliconates is for the in-plant impregnation of roofing tiles. The use of siliconates to impregnate facades has proved unacceptable because the uneven application of the impregnant results in a white layer forming on oversaturated areas and this layer is difficult to remove. Alkali siliconates are also strongly corrosive because commercial siliconates are as corrosive as a 20% potassium hydroxide solution. The alkali metal methylsiliconates are not suitable for the treatment of alkaline substrates which contain free lime and have a pH of 8 or more.[11] Alkali metal propylsiliconates have been developed to treat more alkaline substrates. However, propylsiliconates have limited solubility in water and are very reactive. The necessity to use alcohol/water solvent mixtures to stabilise the propylsiliconates negates the aim of a water-based impregnant.

2.1.2.2. Silanols

Attempts have been made by various workers [23,24,25,26] to produce aqueous silanol solutions from the hydrolysis of alkylalkoxysilanes [$R\text{-}Si(OR')_3$] for impregnating masonry surfaces. When an alkylalkoxysilane is mixed with water thoroughly in the presence of an acid or a base and for a sufficient length of time, a temporarily clear solution of the alkylsilanol [$R\text{-}Si(OH)_3$] may be formed. Alkylsilanol solutions normally contain alcohol, a by-product of the hydrolytic reaction. The problem that arises from the production of silanols is the stability of these solutions during storage. Lower alkylsilanols are water-soluble but condense into water-insoluble alkylsiloxanes. Therefore, clear solutions of monomeric silanols become hazy solutions of undissolved siloxanes in a very short period of time. For these reasons silanols have proven difficult to use for practical purposes.

2.1.2.3. Silane and siloxane emulsions

Aqueous emulsions of organopolysiloxane oils have been developed by Koerner et al.[27] and water-based silicone resin dispersions[28] have also been reported. These emulsions are unsuitable for impregnation of concrete because of the relatively large size of the polysiloxane and the large particle size of the emulsion. They are normally used as hydrophobic additives in plaster, aerated concrete and paints, or as binders in silicone emulsion paints.

De Pasquale and Wilson[29] prepared an aqueous silane emulsion as a masonry water repellent which comprised an alkylalkoxysilane, an emulsifier and water. The emulsifier was the sorbitan of a fatty acid ester having a hydrophilic/lipophilic balance (HLB) value in the range from 4.3 to 11.4. The emulsions prepared in this manner showed acceptable penetration depths and acceptable water absorption values. However, surfaces treated with this emulsion do not exhibit a good beading effect, possibly due to the adsorbed non-ionic surfactant at the surface undergoing rewetting on exposure to water. This effect causes a wetting of the very surface of the substrate and therefore would not be acceptable in freezing climatic conditions. In addition pollutive substances could be carried into the substrate in this wetted layer.

Alkylalkoxysilanes are liable to undergo hydrolysis and a subsequent condensation reaction when incorporated in an emulsion. In order to overcome this problem, Wilson[30] used a buffering agent such as sodium bicarbonate ($NaHCO_3$). The buffering agent enabled the addition of a biocide to the emulsion without a change in the pH of the emulsion.

Deactivatable surfactants are defined as those which decompose and lose their surface active characteristics as a result of an inherent characteristic of the surfactant. This characteristic may be due to a reaction with other materials which are present in a mineral substrate or by a reaction which can be initiated after the impregnation of the mineral substrate. Fatty acid esters, silica esters[31] or esters and alcohol-alkylene adducts[32] have been discussed as deactivatable surfactants by Pühringer. However, the practicability of these ideas was not delineated. The use of an amine soap as a deactivatable surfactant has been used in an industrial process for the treatment of particulates by Raleigh.[33] Silicate particulate matter such as perlite and vermiculite was treated with an emulsion of a polysiloxane with the emulsifier as the ammonium salt of a long chain aliphatic carboxylic acid. The beading effect was activated by heating. Following treatment of the silicate particulate matter, the particles were heated and the silicone fluid formed a coating on the silicate surface and the ammonia evaporated to leave the oily aliphatic carboxylic acid on the surface. This concept had not been adapted to impregnants for masonry.

Heaton[34] invoked the improvement of the beading effect by the addition of a beading additive which provided the desired visual effect of water repellency. He suggested the use of hydrophilic fumed silica, micronised Teflon R, tetrafluoroethylene beads, fatty acid salts, or wax as beading additives. Fey and Freiberg[35] used a fluorosilicone fluid, a polydimethylsiloxane fluid, a room temperature curable silicone rubber, an amine salt functional siloxane copolymer, or a trimethylsilyl endcapped polysilicate in their formulation to improve the surface beading effect on substrates.

In some reported inventions, polymeric additives were used to enhance the shelf life of silane emulsions. Heaton[34] showed that the addition of a water thickening agent such as a neutralised copolymer of an acrylic acid and a long chain alkylmethacrylate increased the emulsion stability and enabled the inclusion of solid particulates as water beading additives to the emulsion.

A method of emulsion polymerisation of cyclic ethylmethylsiloxane or cyclic dimethylsiloxane with strong mineral acids or strong alkaline catalysts was carried out by Hyde and Wehrly.[36] The emulsions were useful for release agents and adaptable for the preparation of latex paints which can be mixed with pigment or other fillers and applied to a surface where the water evaporates leaving a continuous coating. However, the presence of strong mineral acids or strong bases caused a problem in the neutralisation of the emulsion and in the removal of the catalysts. Furthermore, for the best result a separate emulsifying agent needed to be employed in this method and the stability of the emulsions may change when additional materials such as pigments are added. The polymerisation and copolymerisation of silcarbanes were carried out by Findlay and Weyenberg[37] in an aqueous medium where the silcarbanes were in a dispersed state with the presence of a surface active sulphonic acid catalyst. The polymerisation process proceeded at the desired temperature until the desired increase in molecular aggregation was obtained. The organopolysiloxane latex emulsions prepared in this manner were suitable for release coatings. However, they apparently were not stable on storage and could not form a tough elastomer for coating applications. According to Gee,[38] a typical problem encountered with emulsion polymerisation of cyclic polysiloxanes was the presence of an unemulsified silicone oil layer or very large silicone oil droplets in the final product of the process. Complete elimination of the silicone oil layer could not be achieved unless the cyclic siloxane was pre-emulsified using mechanical means prior to polymerisation The author then developed a method of producing a stable and oil-free emulsion which did not contain any unemulsified silicone material and did not produce unemulsified silicone oil or polymers upon ageing. The polymerisation process involved the opening of cyclic siloxane rings using an acid or base catalyst in the presence of water. The products of the opening of the cyclic rings were polysiloxane oligomers with terminal hydroxyl groups. These oligomers then reacted with each other or with other siloxane reactants through a condensation process to form polysiloxane polymers or copolymers. The polysiloxane polymers then precipitated and aggregated to form particles which were stabilised at a specific particle size in water by the ionic and non-ionic surfactants. Polysiloxane latex emulsions are stable and have very fine particle sizes. They are not suitable for the impregnation of concrete. They are added to aqueous paints to make them water repellent and to prolong shelf life. They are also used as binders for silicone paints or added to dry mixes of building materials, e.g. for making high grade, water repellent mortar.

Silane/siloxane emulsions have been developed recently by Schamberg et al.[39] These inventors revealed that the emulsion of a mixture of octyltriethoxysilane and a methylethoxypolysiloxane imparts a better water repellent effect than the effect from emulsions made with either a silane or a siloxane alone. The penetration depth of these emulsions was not significant on concrete substrates. In addition, on neutral substrates the development of water repellent effect was very slow or problematical.

Other research groups have committed significant resources to the research and development of deep penetrating silane emulsions with good surface beading effect with no success.[40,41] This may be attributed to the polar/non-polar nature of silane molecules and the degree of difficulty of obtaining a stable emulsion system with such molecules. Furthermore, the added parameters of achieving limited surface wetting effect from the surfactant together with deep penetration of the active materials present significant obstacles to the researcher.

2.1.2.4. Silane emulsions with silicone surfactants

The difficulty encountered in the art of developing emulsions of polar silane raw materials with limited surfactant wetting effect has encouraged other developments. Goebel et al.[42] have developed new surfactants which are reactive silicone surfactants. These surfactants have been used to develop novel silane emulsions where the surfactant may co-polymerise with the silane base material.

2.1.2.5. Silicone microemulsions

Mayer et al.[43] have developed silicone microemulsions as aqueous masonry water repellents. Silicone microemulsions have the advantage of being solvent-free, stable in concentrate form, easy to use, and have extremely fine-particle size. However, the application in concrete protection has not been widely accepted due to problems of cost (silicone microemulsion requires a large quantity of amino-functional silicone), very short lifetime of the diluted microemulsion and the products do not penetrate very well into concrete substrates.

2.1.2.6. Impregnants for concrete

The present solutions of siliconates or silanols and the present emulsions of siloxanes and silanes do not offer satisfactory water-based impregnants for concrete. Microemulsions have been presented as a valid alternative but the cost, lifetime and performance leave something to be desired. An innovative emulsion has been offered by Goebel et al.[42] but a new class of surfactants had to be synthesised and this presents an obstacle to commercialisation. The silane/siloxane emulsions developed by Schamberg et al.[39] suffer from poor penetration ability and difficulty of development of water repellent effect on neutral substrates.

2.2. Emulsion stability

2.2.1. General considerations of emulsion stability

An emulsion is an heterogeneous system consisting of at least one immiscible liquid dispersed in another in the form of droplets, which are usually within the size range of 0.1 to 100 μm in diameter. Emulsions are inherently unstable systems and the risk of deterioration is higher than with other non-emulsified products and thus stability is considered as the most important physical property of the emulsion in industrial application. There is the added dimension with hydrolysable moieties of chemical stability.

Three interrelated forms of instability commonly encountered in emulsion technology are sedimentation, flocculation, and coalescence. Since the emulsion droplets ordinarily have a density different from that of the dispersing medium, they will tend to accumulate at the bottom or top of the emulsion. Creaming results from the difference in density between the two phases and is related to the attachment of an individual droplet to form flocs or loose assemblies of particles in which the identity of each droplet is still maintained. According to the theoretical calculations by Rybczynski[44] and by Hadamard,[45] the sedimentation rate of a spherical particle in a viscous liquid is given by:

$$v = \frac{2gr^2(d_1 - d_2)}{3\eta_2} \times \frac{\eta_1 + \eta_2}{3\eta_1 + 2\eta_2} \qquad (2.1)$$

where v is the rate of sedimentation, r is the droplet radius, g is the acceleration of gravity, d_1 is the density of the disperse phase, d_2 is the density of the continuous phase, η_1 is the viscosity of the disperse phase, and η_2 is the viscosity of the continuous phase. Equation (2.1) indicates that emulsion stability with respect to creaming, is favoured by small droplets, small differences in density between the disperse and continuous phase, and a high viscosity of the continuous phase.

Flocculation is referred to as the attachment of an individual droplet to form a loose and irregular cluster in which the identity of each droplet is maintained.

Flocculation as well as coalescence increases the effective particle size and thus leads to an increased rate of sedimentation. Forces responsible for flocculation are London-van der Waals attraction forces which are frequently counteracted by electrical repulsion. Flocculation may also be due to the interaction of the flocculating agent with the emulsifier.

Coalescence is a phenomenon in which two or more droplets are joined together to form a larger droplet which has a greater volume, but has a smaller interfacial area. Coalescence cannot take place until two or more droplets are in contact. Therefore, coalescence must be preceded by flocculation. The coalescence rate most likely depends on the film-film surface chemical repulsion and on the degree of irreversibility of film desorption.

2.2.2. Theories of emulsion stability

2.2.2.1. The adsorbed film theory

The effect of the emulsifier on the interfacial tension of the emulsion system has long been recognised. Since emulsions present a large interface area, any reduction in interfacial tension must reduce the driving force towards coalescence and should promote stability. The lowering of the interfacial tension, while important, cannot totally represent the effect of the emulsifying agents. The lowering of interfacial tension by the emulsifying agent facilitates the formation of droplets but does not necessarily increase the stability of the emulsion. In addition, this also does not explain the effectiveness of non-surface active materials, e.g. gums, finely-divided solids and other additives in stabilising emulsions.

The role of the emulsifier in stable emulsions has been studied by Bancroft,[46,47] Harkins,[48] Schulman and Riley[49] and Becher.[50] They indicated that the emulsifying agent is concentrated at the interface and forms an interfacial film which exerts a stabilising influence. The interfacial film is an oriented monomolecular one, with the polar groups oriented towards the water phase and the non-polar hydrocarbon chains oriented towards the oil. Consequently, the droplet will be covered by a more or less dense protecting layer which will hinder the coalescence of the droplets. According to King,[51] the interfacial tension plays a doubtful role in the stability of emulsions, but the interfacial adsorption of the emulsifying agent is vital. King considered that the strength and the compactness of the interfacial film are the most important factors favouring emulsion stability.

Stable emulsions can be prepared by using a combination of two or more emulsifying agents. This phenomenon was studied by Schulman and Cockbain.[52] They showed that mixed emulsifying agents often lead to more stable emulsions due to the formation of a complex film at the water-oil interface. The resulting interfacial film is a closed-packed monolayer which possesses greater strength and resistance to rupture, hence the emulsion droplets would be less liable to coalescence and the emulsion becomes more stable. In contradiction to the observations of Schulman and Cockbain,[52] Kremnev[53] showed that the thixotropic behaviour of mixed emulsifiers plays an important role in the stabilisation of concentrated emulsions. According to Kremnev, highly stable concentrated emulsions of benzene in water could be achieved by the use of thixotropic mixtures of aliphatic alcohols and sodium oleate, owing to their capacity of rapid restoration of the thixotropic structures which were perturbed in the emulsifying process.

Emulsions with greater stability can also be obtained by the use of certain macromolecular emulsifying agents such as proteins, gums, starches and certain synthetic polymers (e.g., polyvinyl alcohol). It has been known that these compounds adsorb at the oil-water interface and because of their multiplicity of hydrophilic and hydrophobic groups, each molecule is attached at many points and therefore are strongly held at the interface. The formation of tough skins between oil and aqueous solutions of macromolecular substances such as gums and proteins have been reported by Serralach and Jones.[54,55] The work of Biswas and Haydon[56,57,58,59] showed that there is a direct correlation between emulsion stability and the visco-elastic parameters of films of emulsifiers formed at the oil-water interface. Nielsen et al.[60] correlated mechanical properties of various macromolecular stabilised interfaces with droplet stability. They chose the "surface rigidity" as the parameter to be studied rather than the elastic modulus.

However, Lawrence[61] has questioned the choice of rigidity as a stabilising factor due to the fact that a rigid film may not be able to "heal" a small disturbance in the interfacial region. It seems probable that an effective macromolecular emulsifier must form an elastic gel, swollen by the continuous phase, and any attempt to thin this gel is opposed by very large osmotic forces.[62]

2.2.2.2. The electrical theory

a. The electrical double layer

Practically, all the particles in aqueous suspensions carry a charge resulting from dissociation of surface groups, adsorption of ions, isomorphic substitution of ions, accumulation (or depletion) of electrons at the surface, and adsorption of polyelectrolytes or charged macromolecular species. The distribution of ions around a charged particle is determined by electrical interaction with the surface and the mixing tendency of thermal motion. Ions with opposite charges (counterions) will be attracted to the surface and can be either closely associated with the surface or distributed in some way into the solution. This leads to the formation of an electrical double layer.

The structure of the electrical double layer is generally regarded as consisting of two regions: an inner, compact layer known as the Stern layer that includes ions bound relatively strongly to the surface by adsorption, and an outer, diffuse layer known as the Gouy (or Gouy-Chapman) layer in which ion distribution is determined by a balance of electrostatic forces and random thermal motion. As particles approach each other, they begin to influence each other as soon as the double layer overlaps. The repulsive electrostatic forces arise from interactions of the surface charges of the particles and the diffuse portions of the electrical double layer as charged particles move closely together . The inner, or Stern layer does not have a direct role in the interactions between surfaces since it has only several molecules of thickness. However, it has a significant indirect role in these interactions in determining the value of the potential of the diffuse portion of the double layer.[63]

Within a low ionic strength solution, the diffuse layer of counterions around the particles extends to a considerable distance and particles begin to repel each other when their diffuse layer overlaps. The repulsion can occur at quite large separations. Within a higher ionic strength solution, the diffuse layer is less extensive and the particles need to approach each other quite closely before repulsion occurs. Interparticle repulsion is an important stabilising mechanism in an oil/water emulsion. This prevents the close approach of the particles or droplets and prevents coalescence.

b. The Derjaguin-Landau and Verwey-Overbeek (DLVO) theory

Colloidal particles present in a dispersion medium are always subject to Brownian motion, and the resultant collisions between particles are frequent. The stability of the system is thus determined by the interaction between the particles during such a collision. Two basic interactions are discernible. One is the electrostatic repulsion and the other is the London-van der Waals attraction between the particles. A colloidal dispersion is only stable when the repulsive force is sufficiently strong to counteract the van der Waals forces.

The repulsion between particles arises from two different sources, one is from the overlap of electrical double layers on the particles, and the other from the interaction between adsorbed layers of non-ionic materials, including adsorbed molecules of the dispersion medium.

A theory relating surface charge to the stability of a colloidal system was developed independently by Derjaguin and Landau[64] and Verwey and Overbeek[65] (the DLVO theory). According to the DLVO theory, the stability of a colloidal system is determined by a balance of the van der Waals attractive energy and the electrical repulsive energy. The total potential energy V_T between the two particles is given by:

$$V_T = V_A + V_R \qquad (2.2)$$

where V_A is the van der Waals attractive potential energy and V_R is the repulsive potential energy.

The London-van der Waals energy for two equal spherical particles is given by[66]:

$$V_A = -\frac{A}{6}\left[\frac{2r^2}{R^2 - 4r^2} + \frac{2r^2}{R^2} + \log_{10}\frac{R^2 - 4r^2}{R^2}\right] \quad (2.3)$$

where r is the radius of the particles, R is the distance between their centres and A is the Hamaker-London constant. For the particles in the medium, the Hamaker-London constant is given by:

$$A = \left(\sqrt{A_{11}} + \sqrt{A_{22}}\right)^2 \quad (2.4)$$

where A_{11} is the Hamaker constant of the particles and A_{22} is that of the medium. A must always be positive, so that there is always an attraction between particles in any medium. For the small particles or emulsion droplets, and in the case of very close approach of the spherical particles (H<<r), the simpler approximation of equation (2.3) is given by:

$$V_A = -Ar/12H \quad (2.5)$$

where H = R-2r is the shortest distance between two spheres. The attraction between particles decreases slowly with increasing interparticle distance. The change in the interaction potential V_A for spherical particles of various diameters with distance of separation may be calculated by substituting numerical values into equation (2.5) with an Hamaker constant A of 10^{-12} ergs. This indicates that the attraction between larger particles is greater than the attraction between the smaller particles.[67]

The interaction between two charged particles was first formulated correctly by Derjaguin and Landau[64] and Verwey and Overbeek.[65] However, the exact equations for the interaction of spherical particles are complex. In the presence of symmetrical electrolytes, the potential energy of repulsion is found to depend on three dimensionless groups:

$$V_R = f\,(\kappa H,\ \kappa r,\ Ze\psi_o/kT) \qquad (2.6)$$

where r is the radius of the particle, H = R-2r is the shortest distance between two spheres, Z is the valency of the symmetrical electrolyte, e is the fundamental unit of electric charge, ψ_o is the surface potential and κ is the Debye-Hückel screening parameter which is proportional to the square root of the ionic strength.

As the interaction of two particles is considered to occur via overlap of the diffuse layer, the strength of the interaction may be determined by the potential at the compact layer and diffuse layer boundary (ψ_δ) and not by the intrinsic surface potential ψ_o. The compact-layer/diffuse layer boundary potential ψ_δ is not directly measurable and electrokinetic, or zeta potential data obtained from microelectrophoresis measurements are normally used as the best approximation available for ψ_δ The zeta potential (ζ) is the potential at the surface of shear between a particle and its diffuse layer which is created as the particle migrates in an applied electric field. It is assumed that the surface shear lies close to the compact layer/diffuse layer boundary and thus ζ and ψ_δ should be very similar. Although the validity of this assumption may be questionable, the advantage of this assumption, however, is that ζ is readily determined experimentally, whereas ψ_δ is not. It is usually held that the zeta potential is a better guide to latex stability than is ψ_o as calculated from the notional surface charge density.[68]

For two identical spheres, the electrical interaction energy, V_E, as a function of the zeta potential can be written in approximate form as follows:[69]

$$V_E = 32\pi\varepsilon r(kT/ze)^2\gamma^2\exp(-\kappa H_o) \qquad (2.7)$$

where z is the valency of the ions and γ is the dimensionless function of the zeta potential $\gamma = \tanh(ze\zeta/4kT)$. Equation (2.7) indicates that the electrical interaction between particles decreases when the zeta potential decreases.

The total interaction between colloidal particles is obtained by the summation of the attraction and the repulsion curves. A schematic total energy of interaction curve is shown in Figure 2.3. The van der Waals attraction is always dominant at closer distances of separation and the attractive energy V_A increases rapidly as the particles approach each other. Under certain circumstances, the electrostatic repulsion can outweigh the van der Waals attraction and give rise to a maximum V_{max} in the total potential energy curve at the distance of separation of the order of 2 nm. The electrostatic repulsion can thus provide an energy barrier which discourages particle contact and since the barrier is of only limited extent, the stabilising effect is kinetic and not thermodynamic in origin. The shapes of the total energy of interaction curves and the height of the primary maximum (or the energy barrier) V_{max} depend on all the parameters that influence V_A and V_R. The surface potential, the ionic strength, the particle radius and the charge on the counterion are considered as the most important of these parameters.[68] The height of the energy barrier V_{max} is considered as the essential activation energy which must be overcome in order to prevent particles adhering. The height of the energy barrier V_{max} can be increased to prevent coagulation by constructing a physical barrier around the particles composed of an adsorbed layer of non-ionic materials. The thicker the layer, the greater the separation between the particles, and hence the colloidal dispersion becomes more stable. This is referred to as steric hindrance of an adsorbed layer.[67]

According to the DLVO theory, the magnitude of the energy barrier V_{max} depends on the dimensions of the particles and their surface potential. With large particles, the total potential energy curve may develop a secondary minimum at an appreciable distance of separation.

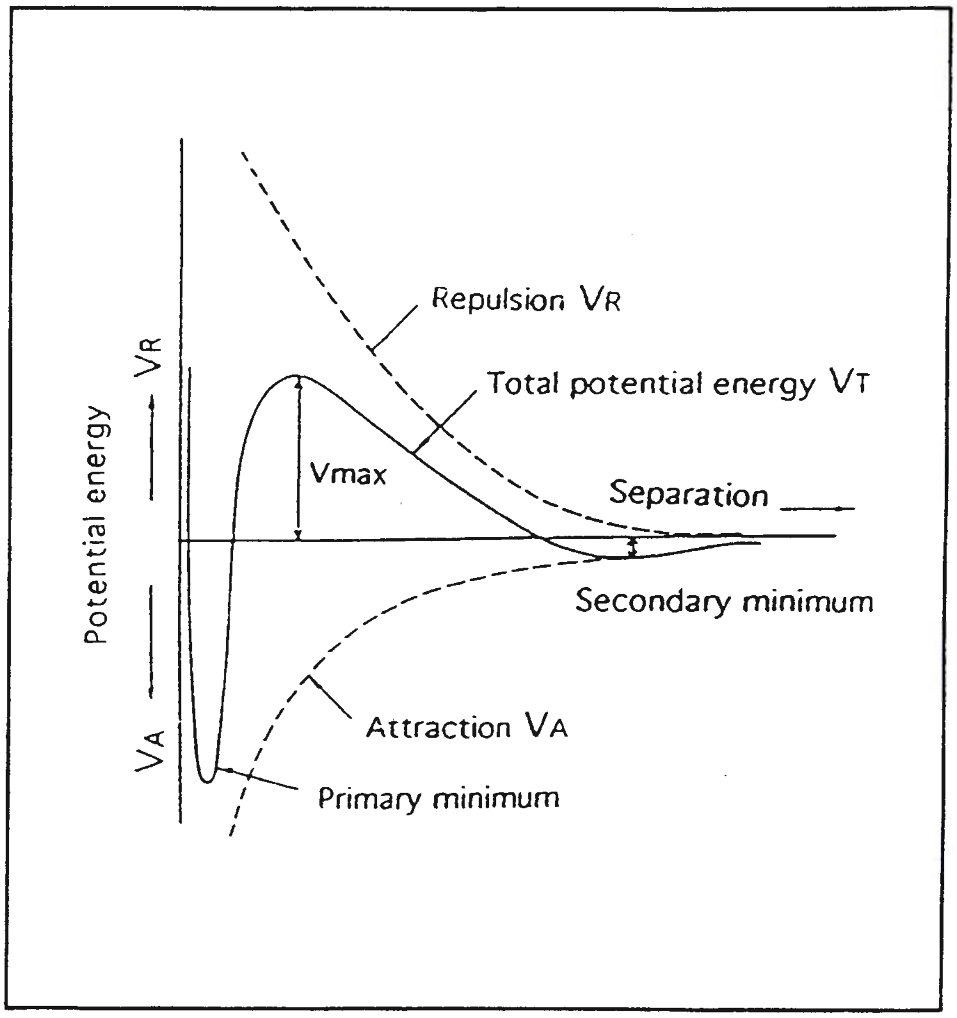


Figure 2.3. Schematic total energy of interaction curve for two particles (Sato, T. and Ruch, R.[67])

If this minimum is several times kT, it should overcome the effect of Brownian motion and give rise to coagulation. The character of this coagulation would be different from that in the primary minimum. The flocculation would be completely reversible and equilibrium distances would be of the order of several times the thickness of the double layer. For colloidal particles of radius of 10^{-6}

cm or smaller, no secondary minimum appears in the total energy of interaction curve and therefore flocculation is not observed.

2.3. Concrete protection through hydrophobicity

2.3.1. Corrosion of steel in concrete

When the reinforcing steel corrodes, the concrete deteriorates. Deterioration of concrete due to corrosion results because the products of the corrosion process build up and occupy a greater volume than the embedded steel, and therefore exert substantial stress on the surrounding concrete. As a consequence, corrosion causes staining, cracking and spalling of the concrete.

The corrosion of steel in concrete is a result of an electrochemical process involving one or more chemical processes and a flow of electricity. The flow of electricity in the electrochemical process is entirely an internally generated one and does not involve any external source of electricity. In electrochemical corrosion in concrete, the galvanic cell is formed in various ways and requires the presence of an electrolyte, that is, water containing dissolved substances whose ions can conduct electricity. Therefore, permanently dry concrete will not support electrochemical corrosion of the embedded steel. Another fundamental requirement for the formation of a galvanic cell is that there must be present two dissimilar metals coupled in the same electrolyte or two similar metals metallically coupled in a different electrolyte. In the latter case, which is of prime importance to the corrosion of steel in concrete, the different electrolyte results from the different concentrations of moisture, oxygen that comes from the air, or dissolved substances existing from place to place in the same concrete structure. The formation of different electrolytes at the anode and cathode is due to the differences in permeability of the concrete in anodic and cathodic regions. Even in concrete which is of uniform permeability, the difference in salt concentration in anodic and cathodic regions still exists due to differences in the environments to which various parts of the concrete members are exposed. The two metallic surfaces in different electrolytes act as cell electrodes in the concrete structure. The metallic surface where the protective film in concrete is poor will act as an anode while the metallic surface where there is a good protective film will act as a cathode. Electron current will flow from the anode to the cathode through the embedded steel then through the electrolyte back to the anode to complete the electrical circuit. The principal chemical reaction at the anode is as shown in equation (2.8)

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (2.8)$$

The iron ions react further with water and oxygen that are present in the concrete to from rust. The chemical reactions at the cathode may vary depending on circumstances, but the principal one related to the corrosion of steel in concrete is as shown in equation (2.9)

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (2.9)$$

The rate of this reaction is affected by different factors such as the relative size of the electrodes, the concentration of oxygen, the temperature, and the electrical resistivity of the electrolyte. The corrosion of reinforcing steel in concrete will not take place if for any reason, the chemical reactions at the electrodes do not occur and the galvanic cell does not operate.

2.3.2. Factors causing reinforcing steel corrosion

Corrosion in reinforced steel in concrete is affected by various factors such as chloride ion, carbon dioxide, oxygen and water.[7]

Chloride ion is the most prevalent and damaging cause of corrosion of reinforcing steel in concrete. Chloride ions are introduced into concrete in a variety of ways. They are intentionally added as an accelerating admixture (such as $CaCl_2$), accidentally included as contaminants in aggregates or penetrate the concrete from de-icing salts, marine environment, fog or mist. Concrete normally provides a high degree of protection against corrosion to embedded steel due to the formation of a thin protective film of gamma iron oxide on the steel surface. However, this passivating film is destroyed when sufficient salt (chloride ion) penetrates to the steel surface. It is well known that even very small concentrations of chloride ions can break the passivating film. Chlorides may be present in concrete in a number of states. However, it is believed that only the free chloride ions influence the degradation of reinforced concrete by causing corrosion of embedded steel.[70]

Carbon dioxide (CO_2) plays a dominant part in damaging reinforced concrete. It is present at a high concentration in the atmosphere. When concrete contacts carbon dioxide from the air or carbon dioxide dissolved in water, carbonation occurs. Carbonation is the effect of carbon dioxide in the air on Portland cement products, mainly calcium hydroxide [$Ca(OH)_2$] in the presence of moisture. The $Ca(OH)_2$ is converted to calcium carbonate [$CaCO_3$] by absorption of CO_2.

$$Ca(OH)_2 + CO_2 + H_2O \longrightarrow CaCO_3 + 2H_2O \qquad (2.10)$$

Carbonation reduces the pH value of the concrete from around 12 to 9 and below. If the carbonation zone reaches the steel at this low pH, the passivity of the steel surface in the concrete is destroyed and corrosion of steel is likely to start. Carbonation proceeds from the surface of the concrete inwards and the rate of the carbonation process is extremely slow. It has been shown by Tutti[71] and Lawrence[72] that carbonation takes place on the exposed surface and gradually moves into the concrete. The rate of progress of the carbonation front is proportional to the square root of time ($\sqrt{t}$).

Carbonation of concrete exposed to the atmosphere is inevitable, but its significance to the durability of reinforced concrete is only important under certain conditions. If the cover zone of the embedded steel is permeable and the cover depth is low, then the carbonation front can reach the reinforcement in a relatively short period of time . The presence of chlorides, even in an alkaline environment will exacerbate the corrosion process. The actual rate of carbonation depends on the permeability of the concrete, its moisture content, the concentration of carbon dioxide in the surrounding environment and the relative humidity of the ambient medium. The moisture content is considered to be a very important factor which causes the corrosion of the reinforcing steel in carbonated concrete. It has been shown by the work of Volkwein and Springenschmid[6] in Germany that even if the concrete was carbonated, in dry concrete, corrosion was not exhibited. This was confirmed by ACI Committee 222 Report,[7] which indicated that in the interior of buildings, carbonation of the concrete past the embedded steel can occur with no resultant corrosion due to the dry state of concrete.

Corrosion of steel in concrete is an electrochemical process and the availability of oxygen at the cathode is one of the main factors for the chemical reaction. In a cathodic reaction, the oxygen has to be in a dissolved state. According to González et al.,[73] oxygen diffusion alone will not accelerate the corrosion rate and the corrosion mechanism in some cases does not require oxygen diffusion.

Concrete absorbs water through its capillaries and pores. Water absorption increases the moisture content in concrete. Through the capillary system, water conveys harmful substances such as salts into concrete, which can cause severe damage to the embedded steel. It has been reported that the majority of damage to concrete bridges is caused by the penetration of contaminated water through the cover to the embedded steel.[74]

The electrical resistivity of the concrete depends on the moisture content of the concrete. Dry concrete has been found to have a higher resistivity than water-saturated concrete. Gjørv et al.[1] indicated that progressive drying of initially water-saturated concrete results in electrical resistivity increasing from about 7×10^3 ohm.cm to about 600×10^3 ohm.cm. Field observations by Tremper et al.[2] indicated that when the resistivity exceeds a level of 50 to 70×10^3 ohm.cm, steel corrosion would be negligible. Browne[3] quoted values of resistivity of 10×10^3 ohm.cm whilst Cavalier and Vassie[4] quoted the value of 12×10^3 ohm.cm above which corrosion induced damage is unlikely even in the presence of chloride ions, oxygen, and moisture. The work of Browne,[3] Cavalier and Vassie,[4] and Wiss, Janney, Elstner Associates[5] showed that when the concrete is kept dry, corrosion of the embedded steel is very slow or insignificant, even in the presence of significant chloride ion concentrations. This insignificant corrosion rate in dry concrete is due to the corrosion reaction not having the electrolyte portion available to support the ionic conduction of current in the corrosion cell. Diagnostic studies on concrete in the field by Volkwein and Springenschmid[6] also showed that even if the concrete was carbonated, corrosion of the embedded steel was not apparent if the concrete was dry. Therefore, the "keeping dry" effect has been shown to significantly reduce corrosion when the concrete is contaminated with chloride ions or when the concrete is carbonated.

2.3.3. Protective measures for reinforcing steel

Several strategies have been developed to inhibit corrosion of reinforcing steel. These strategies are based largely on work that has been done in recent years on bridge-deck problems. The possible strategies include protective coatings on the embedded steel, suppression of the electrochemical process (cathodic protection), protective surface coating of the concrete surface and protective impregnation of the concrete surface.

2.3.3.1. Reinforcement protection

Many substances are used as additives to concrete to inhibit corrosion of the reinforcing steel. Such chemicals may act either to suppress the anodic reaction by stabilising the passive oxide film or by forming a new insoluble coating (chromates, phosphates), or to suppress the cathodic reaction by scavenging oxygen (nitrites, benzoates, stannous and ferrous salts).[75] However, when used in quantities sufficient to be effective in inhibiting corrosion, some of these substances may seriously reduce the concrete strength. In addition, when used in sufficient concentration to deliver an effect the cost may be significant as they are added to the bulk concrete.

Protective coatings of reinforcing steel in concrete structures has been recommended to protect reinforcing steel from corrosion. Metal coatings, such as zinc galvanising, are often used to protect steel from corrosion and galvanised reinforcing bars have been used successfully in concrete. Other metals, such as cadmium, nickel, and copper have also been tested. Zinc and cadmium provide sacrificial anodic protection because they are more prone to corrosion and act as anodes, making the iron cathodic.[76] The protection of the reinforcing steel by such metal coatings may be insufficient in the presence of chloride ions, which accelerate the corrosion of the coatings. The corrosion products may themselves cause distress in concrete, and protection ceases when all the metal is consumed. Nickel and copper act as inert coatings at high pH, although they, too, can be susceptible to corrosion in the presence of chloride ions. Holes or scratches in the metal coating film could lead to undue corrosion of the metal at that point, and thus, deplete it. Furthermore, cut ends of the galvanised bars will produce the same effect.

Inert coatings such as epoxy resins, asphalt, and synthetic rubbers have been used. Epoxy resin coatings, however, can only provide good protection to reinforced steel if the concrete is placed before the resin hardens and this procedure is obviously not always practical. Bituminous and asphaltic coatings have the disadvantage of considerably decreasing the bond between the reinforcing steel and concrete. The effectiveness of reinforcing coatings depends on their integrity during fabrication and their bonding to the embedded steel. Damage to the coating during transportation of the steel and handling during the erection of the structure affect the value of this approach.

Cathodic protection is generally used for protecting repairs to an already corroding structure rather than being installed during construction. However, some major high value structures such as offshore installations have embodied a cathodic protection system from their inception. Cathodic protection based on the impressed current method has been applied on occasions to both ordinary concrete and prestressed concrete structures.[77] According to Gjørv,[78] the difficulties in using this method are to determine the correct potentials to apply to the system and to make sure that it is applied uniformly over the entire reinforcement. As the electrical resistivity of the concrete is highly dependent on the moisture and salt content in the concrete, the electrolytic conditions may vary noticeably from part to part within the same structure, as well as from time to time depending on the environmental conditions. Furthermore, the applied voltages must not be too high, since the excessive alkali may then lead to a softening and a breakdown of the bond between the steel and concrete. Hausmann[79] has set some criteria for the application of cathodic protection. However, the practical experiences with cathodic protection are very limited and it has not been used generally on concrete structures.

2.3.3.2. Hydrophobic additives

Hydrophobicity of a concrete substrate is achieved by adding hydrophobic additives to the concrete mix, applying a protective coating to the concrete surface or impregnating the concrete with water repellent materials.

The use of hydrophobic additives may control the permeability of the substrate and reduce the ingress of external water, thus, reducing the risk of corrosion of the reinforcing steel. The hydrophobic additives are added directly to the concrete mix and the chemical materials are able to form a thin hydrophobic layer within pores and voids and on the surfaces of concrete by reaction with cement hydration products or by coalescence on contact with cement products.[80] Hydrophobic additives are used normally for improving the quality of concrete bricks, blocks and cladding panels where the benefits are reduced efflorescence and the maintenance of clean surfaces. More even drying out of adjacent bricks and panels is also obtained. In water-retaining structures or basement concrete subject to high hydrostatic pressure, they are generally not beneficial.

2.3.3.3. Protective surface coating

Surface treatment is the other major method of preventing corrosion by excluding external sources of corrosive influence from the concrete. The concrete member is isolated from the corrosive environment by a surface coating where the aim is to exclude liquid water and carbon dioxide or by a hydrophobic impregnation to effectively exclude liquid water. It is possible to combine the two approaches and impregnate followed by a surface coating.

Surface coating materials for concrete include polyurethanes, epoxies and paints based on acrylic resins or acrylic resin/siloxane compounds as binders. These materials form a coating on the concrete and slow down the rate of deterioration by reducing the moisture content, and acting as a barrier to the choride ions and carbon dioxide. Surface coatings are considered as a reliable way of protecting concrete and decorating new concrete or enhancing the poor appearance of concrete which has been repaired in different places. A good surface coating is only obtained if the coating adheres well to the surface of concrete.

Surface coatings seal the surface capillaries or at least greatly reduce their diameter and hence, allow water to build up behind the coating if water can enter the concrete from another source and cause the coating to blister and dis-adhere. In general, pigmented coatings provide better protection and are more durable than unpigmented coatings. Therefore, surface coatings usually impart colour or a change of colour to the concrete. The life of the coatings themselves is difficult to predict and certainly the coatings will not last as long as a durable concrete surface and the recoating of concrete from time to time is unavoidable.

2.3.3.4. Protective surface impregnation

Concrete may be imparted with water repellency by impregnating it with suitable compounds. Water repellency is achieved by coating the walls of the capillaries and micropores with a very thin layer of water repellent material which prevents wetting and water absorption by a surface tension effect. The capillaries and pores of the treated concrete lose their absorbency and the treated concrete becomes water repellent. Unlike surface coating, the pores and capillaries of the concrete treated by surface impregnation are not blocked. Therefore the permeability to water vapour of the treated concrete is generally not significantly reduced.

CHAPTER THREE

Materials, equipment and test procedures

3.1. Materials

3.1.1. Alkylalkoxysilanes

The alkylalkoxysilanes used in the experiments were commercial isobutyltrimethoxysilane (IBTMS), isobutyltriethoxysilane (IBTES) and n-octyltriethoxysilane (OTES). IBTMS was supplied by Dynamit Nobel Chemie (U.K) Ltd. under the tradename Dynasylan BSM. IBTES was supplied by Hüls A G under the tradename Dynasylan BHN and OTES was supplied by PCR Incorporated under the tradename Prosil 9206. These silanes were used without further purification.

3.1.2. Surfactants

3.1.2.1. Alkylbenzenesulphonic acid

Alkylbenzenesulphonic acid was supplied by Albright & Wilson (Australia) Limited under the trade name Nansa SSA/S. The acid contained about 1% sulphuric acid and 2.5% other impurities.

3.1.2.2. Sodium dodecylbenzenesulphonate

Technical grade sodium dodecylbenzenesulphonate was supplied by the Aldrich Chemical Company, Inc.

3.1.2.3. Amine soap

The raw materials for the *in situ* formation of amine soap at the interface during the emulsification process were technical grade fatty acids and an amine such as morpholine or ammonia. The fatty acids included oleic acid and linoleic acid. These were supplied by the Aldrich Chemical Company Inc.

3.1.3. Silicone fluid

Commercial silicone fluid used in this study was a polydimethylsiloxane polymer with trimethylsiloxy termination and having a viscosity of 350 cps. The fluid was provided by Dow Corning Australia Pty Ltd.

3.1.4. Octyl/methyl methoxysiloxane

Commercial octyl/methyl methoxysiloxane was supplied by Wacker-Chemie GmbH under the trade name Wacker VP 1268.

3.2. Equipment

3.2.1. Emulsion polymerisation reactor

The emulsion polymerisation of IBTMS was carried out in a three neck flask. The reaction vessel was equipped with a mechanical stirrer of variable speed, a thermometer and a gas inlet. The temperature of the system was maintained by a constant temperature bath.

3.2.2. Sorvall RC5C centrifuge

A Sorvall RC5C centrifuge with controlled temperature was used to purify the latex particles. The centrifuge operated at 9,000 rpm and the temperature of the latex sample was maintained at 10°C for 30 minutes. A maximum quantity of 2400g of latex was centrifuged each time.

3.2.3. IKA Ultra Turrax T25 shear mixer

Emulsions were prepared in a 500 ml glass fleaker, using an IKA Ultra Turrax T25 shear mixer with a S25N-18G dispersing tool. The fleaker was cooled with running water during the emulsification process. The shear mixer was operated at different speeds of 8000, 9500, 13,500, 20,500 or 24,500 rpm.

3.2.4. Cambridge Du Nouy tensiometer

A Cambridge Du Nouy tensiometer was employed to measure the surface tension of the polysiloxane latex at different concentrations. The ring method was employed for measuring the surface tension of the polyisobutylsiloxane

(PIBS) latex. The instrument used a fine torsion wire to apply the necessary force required to pull on a platinum ring from the surface of the liquid under investigation. Calibration was carried out prior to any tests and the results were reproducible to 0.1 dynes/cm.

3.2.5. Malvern Mastersizer

The study of particle size distribution of the PIBS latex and silane/siloxane emulsions was undertaken with the use of the Malvern Mastersizer Model MS 20. Samples were diluted in distilled water and the particle size distributions were analysed by a computer using Mastersizer S3.01 software.

3.2.6. DV-I Brookfield digital viscometer

The Brookfield digital viscometer model DV-I was used for the measurement of the viscosities of the PIBS latex and silane/siloxane emulsions. The UL Adapter accessory was used in combination with the Brookfield viscometer to obtain accurate and reproducible measurements on low viscosity materials. The flow jacket of the adapter was connected with a circulating temperature bath so that precise sample temperature control could be achieved. Calibration with standard silicone fluids was carried out prior to viscosity measurement.

3.2.7. Malvern Zetasizer 4

Zeta potentials of the PIBS latexes and the novel silane/siloxane emulsions were measured using a Malvern Zetasizer 4 Analyser. The system consisted of three components: the optical unit, the correlator series 7032 Multi-B, and the computer using PCS-Zeta Mode V1.23 software to analyse data. Samples were diluted in distilled water then injected into the cell. Five measurements were carried out for each sample at a measuring interval of 30 seconds and the operating parameters were as follows:

Cell type	AZ 104
Cell temperature	25 ^{0}C
Cell position	14.6 %
Applied voltage	150 Volts
Refraction index	1.333
Dielectric constant	79

3.2.8. Headspace GC-MS chromatograph

The silane and alcohol content in emulsions were determined by gas chromatograph headspace analysis. The emulsion samples were heated at 80°C in a thermostat controlled oil bath of the Hewlett Packard 13395-A Headspace Sampler. The headspace vapours were then carried by Helium gas to a Hewlett

Packard 5890 Series II Gas Chromatograph with a HP 5971A Mass Selective Detector. The mass spectral data acquired from the gas chromatograph was then analysed by the HP-G1030A MS Chem Station (DOS Series), using HP-G1034B Software. The operating conditions for the analysis were as follows:

Headspace conditions:
Method: 1
Bath temperature: 80^{0}C
Valve/Loop temperature: 90^{0}C
Sampling interval: 30 min
Method sequence: 1, 2
Carrier flow (He): 160 ml/min
Auxiliary pressure (He): 1.5 bar

G C conditions:
Column: 25 QC2 BP20 - 0.25 μm
(a) Thickness: 0.25 μm
(b) Dimension: 0.22 mm ID; 25m
Carrier gas (He): 0.8 ml/min
Oven temp.: 35^{0}C
Inlet temp.: 250^{0}C
Duration of analysis: 12.5 min

A standard curve was constructed by plotting the peak area against the concentration of ethanol standard solutions.

3.2.9. Gel permeation chromatograph

Molecular weight distribution of PIBS latexes were studied using gel permeation chromatography (GPC). The instrument consisted of (a) a Bio-Rad HPLC pump model 1330, (b) a series of Ultrastyragel^{TM} 500 A° and

Ultrastyragel^{TM} 100 A^{o} (Waters Associates Inc.) columns and (c) an Evaporative Light Scattering Detector (ELSD)-VAREX MK III (Alltech Associates Inc.). The solvent used for the GPC analysis was tetrahydrofuran (THF) and the concentration of the sample was 0.01 per cent by weight in THF. A calibration curve was established by plotting the elution volume of the peak maxima of a series of polystyrene standards with polydispersities (ratio of M_w to M_n) of less than 1.1 against their molecular weight. The operating conditions for the GPC analysis were as follows:

Injection volume:	20 μl
Flow rate:	1 ml/min.
Nitrogen gas flow rate:	2.5 Standard litres per minute (SLPM).
Drift tube temperature:	60 °C.
Attenuation:	2
Standards:	0.01 % polystyrene standard in THF

3.2.10. Orion pH/ISE meter model 720-A

An Orion chloride ion electrode model 96-17B and a digital benchtop pH/ISE meter model 720A were used to measure directly the chloride concentration in various test solutions. The test solution was acidified to pH 4 with 1M HNO_3 to minimise hydroxide interference. The ionic strengths of standard solutions and test solutions were adjusted by the addition of 2 ml of 5M $NaNO_3$ per 100 ml solution. The meter was initially calibrated using three aqueous solutions of known chloride concentrations before the measurement of the chloride concentration of the samples. Calibration was undertaken with one standard every two hours to compensate for possible electrode drift. The slope of the electrode was -57.9 mV at room temperature. The blank was automatically corrected and the chloride concentration of the samples was calculated automatically and displayed on the meter.

3.2.11. ^{29}Si NMR spectrometer

Silicone nuclear magnetic resonance (^{29}Si NMR) spectra of isobutyltrimethoxysilane monomer and polyisobutylsiloxane polymer were recorded using a Bruker DPX300 Spectrometer. The ^{29}Si NMR spectra were acquired at 59.595 MHz by using inverse gated decoupling measurement. Samples were dissolved in deuterated chloroform ($CDCl_3$) before NMR analysis. Each spectrum was obtained after 100 scans and tetramethylsilane (TMS) was used as internal reference.

3.2.12. QUV accelerated weathering tester

The relative durability of impregnated concrete specimens subjected to the attack of UV light or moisture was tested with the QUV accelerated weathering tester. The impregnated concrete specimens of size 75×105×30 mm were exposed to concentrated UV light and pure water at controlled elevated temperature in a test chamber during 1500 hours.

The QUV tester was operated with repetitive cycles of 4 hours of UV radiation at 60°C followed by 4 hours condensation at 50°C. The possible deterioration such as chalking, cracking, blistering, colour change and water repellency loss were examined. The QUV test data was used to evaluate the performance and the efficacy of the novel silane/siloxane emulsions in concrete protection in comparison to the comparable solvent-based silane solutions.

3.3. Preparation of silane/siloxane emulsions

The siloxane used for the preparation of novel silane/siloxane emulsions in this study was either polyisobutylsiloxane (PIBS) which was prepared in the form of a latex, or commercial polydimethylsiloxane (PDMS). The concentration of the siloxane in the novel emulsions depended on the structure and the molecular weight of the siloxane and the type and concentration of the surfactant used.

3.3.1. Preparation of polyisobutylsiloxane (PIBS) latex

Alkylbenzenesulphonic acid (ABSA) and 70 grams of distilled water were mixed and stirred in a reaction vessel to give a solution of pH equal to 1.5. 28 Grams of isobutyltrimethoxysilane (IBTMS) was added into the acid solution and the hydrolysis of IBTMS was completed in about 15 minutes under moderate stirring. 2 Grams of sodium dodecylbenzenesulphonate (SDBS) was then added into the reaction vessel to adjust the pH of the solution to 3-4 and the system was heated to 35°C. Methanol produced by the hydrolysis of IBTMS was removed during the emulsion polymerisation process via slow evaporation in the fume cupboard. Alternatively, the removal of methanol could be carried out by purging with nitrogen through a gas inlet of the reactor. The system became a milky solution and the condensation polymerisation of the isobutylsilantriols (IBST) started after 20 minutes. The reaction was allowed to continue for 24 hours at a constant temperature to achieve the desired latex whose particle size was suitable for the making of silane/siloxane emulsions in the subsequent process.

The prepared PIBS latex contained other materials such as some of the emulsifier molecules which were not adsorbed at the surface of the latex particles and were soluble in the aqueous phase, and polymerised coagulum which was unemulsified silicone resin. Therefore, the removal of part or all of the above ingredients which were considered as impurities must be carried out meticulously. A number of cleaning methods have been developed to "clean" latex systems. These methods include dialysis [81,82] and hollow-fibre dialysis [83], ion-exchange,[84,85,86] gel filtration,[87] activated charcoal,[88] centrifugation,[89,90,91] serum replacement,[92,93,94] diafiltration,[95] and microfiltration.[96] In this research, centrifugation which has been widely used for cleaning latex systems was used for cleaning the PIBS latex. The PIBS latex obtained from the emulsion polymerisation process was filtered through glass wool to remove latex coagulum. The filtrate was then centrifuged for approximately 60 minutes to separate the polymer particles from residual surfactant and unreacted monomers, using the Sorvall RC5C centrifuge at a speed of 5000 rpm and at a temperature of 10°C. The polymer particles were then washed again with distilled water and redispersed in distilled water to obtain the final PIBS latex with the desired concentration of solid. The process of redispersion of the sediment particles into distilled water and recentrifugation could be repeated several times for the complete cleaning of the latex system.

The centrifuge process could also be carried out at a higher speed of 9,000 rpm and in about 30 minutes. The PIBS latex prepared by the method of this research can be stored for a substantial time at a solids concentration up to 50% by weight without a change in its properties.

3.3.2. Preparation of PIBS latex/silane emulsions

PIBS latex/silane emulsions were prepared as concentrates which contained 40 per cent by weight of the active alkylalkoxysilane, and 60 percent of the PIBS latex containing 30 per cent solids.

60 Grams of PIBS latex was introduced into a 500 ml glass fleaker and neutralised with morpholine. 40 Grams of commercial alkylalkoxysilane was then added to the fleaker and the system was sheared at a speed of 20,500 rpm for 20 minutes, using an IKA Ultra Turrax T25 shear mixer with a S25N-18G dispersing tool. The system was cooled with running water during the emulsification process.

3.3.3. Preparation of PDMS/silane emulsions

The preparation of the PDMS/silane emulsions was carried out as follows: Ten grams of commercial polydimethylsiloxane was introduced into a solution of 1 gram of oleic acid and 49 grams of distilled water which was neutralised with ammonia to a pH of approximately 7. In this procedure ammonia could be substituted with morpholine. 40 Grams of alkylalkoxysilane was then added to the mixture and the system was stirred at a speed of 24,500 rpm for 10 minutes, using an IKA Ultra Turrax T25 shear mixer with a S25N-18G dispersing tool.

3.4. Test procedures

3.4.1. Freeze-thaw stability test

Freeze-thaw resistance tests for the PIBS latex and the novel silane/siloxane emulsions were carried out according to ASTM D2243 Standard Test Method. Samples were stored in a test chamber maintained at -18°C in such a manner that free circulation of air was permitted around each container. For a 24 hour freeze-thaw cycle, the test samples were kept in the chamber for 17 hours and then removed and allowed to stand undisturbed at room temperature for 7 hours, adjacent to the control samples. The procedure was repeated three times and each sample was tested in duplicate. After completion of three cycles, the samples were then observed for any sign of settling and coagulation.

3.4.2. Preparation of test specimens

Concrete was prepared in the laboratory with the following mix proportions (in kg/m^3):

Cement		281
Water		180
Aggregate		
	Coarse (20 mm)	410
	Fine (10 mm)	680.

These mix proportions represent a typical medium grade concrete which had an average compressive strength of 28.5 N/mm^2 after 28 days. The mix was cast into slabs of 500×500×45 mm which were cured for 28 days. These concrete slabs were then cut into cubes with dimensions 50×50×45 mm. The surface of the concrete cube to be treated was always the same.

Cylindrical cement mortar blocks with dimensions of 75 mm diameter and 30 mm length were prepared in the laboratory according to British Standard (BS 6477) in which the cement/sand/water ratio was 1: 4.5: 0.6. They were cured at room temperature for 28 days before testing.

The substrate surface was washed with water using a metal brush, dried in an oven at 105^{0}C and then allowed to cool to room temperature before impregnation. One side of the specimen was immersed in the emulsion or solution (Figure 3.1) containing different concentrations of alkylalkoxysilane. The time of immersion was 60 seconds in each case.

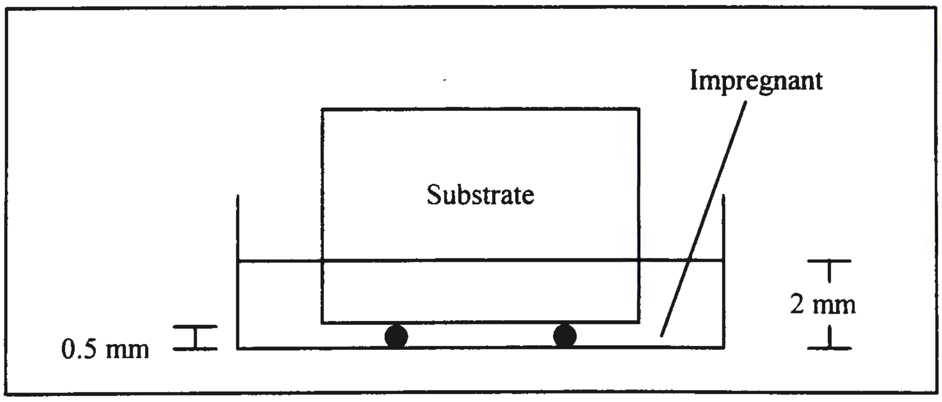


Figure 3.1. Impregnation of the test sample

3.4.3. Beading effect examination

The beading effect was determined according to Schamberg et al.[39] The treated substrate was cured for 7 days after impregnation before it was subjected to water beading examination. About 0.2 ml of tap water was dropped horizontally onto the test surface with a pipette. After 10 minutes, the water on the surface was then removed and the contact area of the water droplet and the surface was evaluated visually and graded according to the following standard:

1 No wetting of the contact area

2 50% of the contact area wetted

3 100% of the contact area wetted

4 Part of the water droplet (less than 50%) absorbed

5 50% or more of the water droplet absorbed

6 Water droplet absorbed completely

7 Water droplet completely absorbed in less than 5 minutes.

3.4.4. Measurement of penetration depth

After impregnation with the water repellent liquid, the test samples were stored for seven days for curing. The depth of penetration was measured by breaking the impregnated blocks in half and wetting the fractured surfaces with water. The bright edge (unwetted) of the cross-section was then measured as the penetration depth of the impregnant.

3.4.5. Water absorption test

The impregnated concrete blocks were stored for two weeks at room temperature before their initial weights were recorded. The treated blocks were then placed on a saturated sponge in a water bath according to DIN 52617E (Figure 3.2). After sitting on the saturated sponge for a period of time, the test blocks were removed, blotted dry and immediately weighed. The percent weight gain of each concrete block was determined by following equation:

$$\%\ \text{Weight gain} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}} \times 100$$

The water absorption of the treated blocks was determined through testing over a period of 35 days.

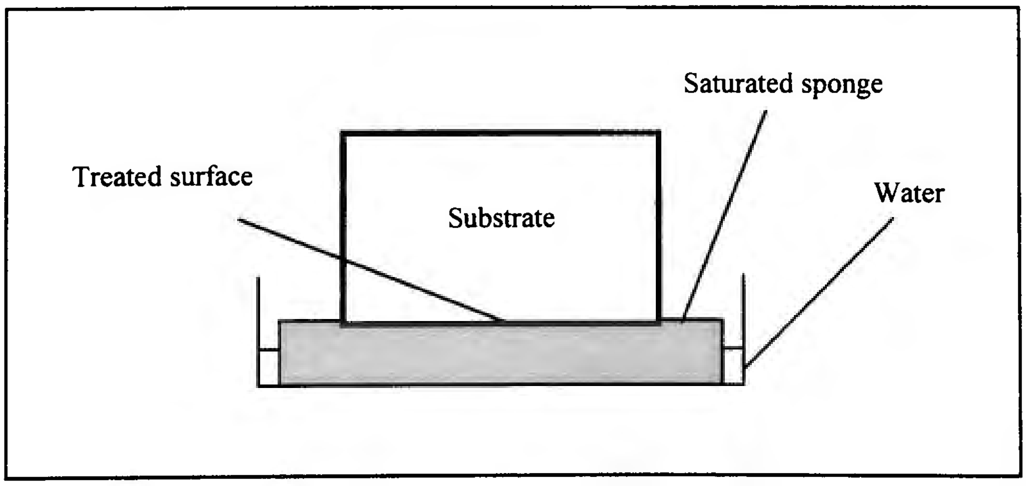


Figure 3.2. Water absorption test of treated substrate

3.4.6. Alkali stability test

The test procedure was carried out using a similar procedure to the water absorption test. The treated blocks were placed on a saturated sponge in a water bath containing 0.1 M KOH solution. The percent weight gain of each block was then determined through testing over a period of 35 days.

3.4.7. Chloride ion resistance test

One side of a concrete block of dimensions 100×100×130 mm was immersed in the silane solutions or silane/siloxane emulsions for 60 seconds. These specimens were then cured for 28 days. Four sides of the block were then sealed with epoxy coating to prevent test solution entering the block from these sides. The blocks were placed in a trough containing 3% NaCl solution so that they were standing in 1.5 cm solution on the treated side for 35 days. The concrete blocks were removed from the solution and kept in laboratory conditions for one week. To determine the chloride content and its change with time in the controlled environment, cylindrical core specimens of 50 mm in diameter were taken by drilling downwards perpendicular from the centre of the treated surface to the opposite untreated surface. The cylindrical core specimen was cut into discs at a depth of 2,4,6,8,10 cm below the treated surface. The concrete disc was then crushed into fine powder with a ring mill. One gram of the concrete powder was mixed with 100 ml of deionised water and the chloride content in the solution was determined using the chloride electrode.

3.4.8. Efflorescence resistance test

The test procedure was carried out using a similar procedure to the alkali stability test. The treated concrete blocks were placed with the untreated surface downward at a depth of 15 mm in a trough containing 10% aqueous sodium sulphate solution so that they were standing at 0.5 mm above the bottom of the trough. After 14 days, the test samples were examined visually for any sign of efflorescence on the treated surface.

CHAPTER FOUR

Siloxanes for silane/siloxane emulsions and the preparation of polyisobutylsiloxane latex

4.1. The use of siloxane for the preparation of novel emulsions

Silanes are known to be difficult molecules from which to achieve stable emulsions. This is due to their polar/non-polar nature and their low viscosity. It is possible to produce silane emulsions with non-ionic surfactant as the emulsifier as reported for instance by De Pasquale and Wilson.[29] The level of surfactant necessary to achieve a stable emulsion produces a wetting effect on treated concrete substrates. Investigation of a range of non-ionic surfactants with a variety of silanes in the present study confirmed the difficulty of achieving a satisfactorily high concentration silane emulsion in terms of stability and performance.

The polarity and viscosity of the organic phase of the emulsion may be adjusted by the addition of oligomeric silanes. This was investigated in the present study by the use of mixtures of silanes and octyl/methyl methoxysiloxane (BS1268). The use of such silane/oligomeric silane mixtures as the oil phase for the emulsion did not produce success in terms of the parameters of stability and performance for high concentration silane emulsions. The use of amine soap surfactants within this system also did not provide satisfactory emulsions. Therefore, in order to develop a novel silane/siloxane emulsion, it was necessary to prepare a suitable polysiloxane to add to the base silane and surfactant. This can be achieved by using a commercial siloxane or by polymerisation of a monomeric silane.

The use of commercial silicone fluids to prepare novel silane/siloxane emulsions has been investigated in this study with the intention of solving the stability problem related to the viscosity of the oil phase and to simplify the preparation process. Silicone fluids containing large alkyl substituents are not commercially available and thus, commercial polydimethysiloxanes (PDMS) with molecular weights in the range of 3780 to 28,000 have been used. In order to minimise the unfavourable effect of the methyl group on the performance of the PDMS/silane emulsions, the concentration of the PDMS was minimised and amine soap was used as an emulsifier. It was found that a commercial PDMS with trimethylsiloxy termination having a molecular weight of 13,650 was the preferred siloxane for the preparation of PDMS/silane emulsions with the amine soap as surfactant.

Consideration of the parameters of the target silane emulsion required that the desired polysiloxane obtained by polymerisation for use with the silane as the oil phase should be alkali stable. In general, methyl silicone polymers are not alkali stable (see Chapter 6). Therefore, the use of a methyl silane as the monomer for polymerisation was not a satisfactory choice. The choice of silane rested with propylsilane, butylsilane or octylsilane. The propylsilicone polymer would not achieve comparable alkali stability to those from butyl or octylsilanes so it was discarded as a choice. This left butyl or octyl as the alkyl substituent on silicone. It was considered that the octyl substituent may be too bulky and hydrolysis of the esters of octylsilane are known to be difficult. Therefore, isobutyl was chosen as the alkyl group. The methyl ester was chosen due to the ease of hydrolysis in the acidic conditions of the polymerisation reaction. Isobutyltrimethoxysilane was therefore chosen as the monomeric silane to investigate for polymerisation to a polysiloxane additive (PIBS) possibly suitable for preparation of the silane/siloxane emulsion.

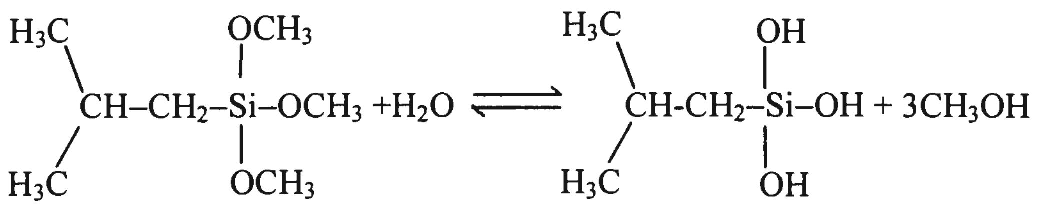
It was found in this study that stable silane/siloxane emulsions could be prepared from a polyisobutylsiloxane (PIBS) latex and an alkylalkoxysilane. The use of PIBS latex for the development of novel silane/siloxane emulsions has several advantages. The latex produced from the emulsion polymerisation of IBTMS was employed directly for the preparation of silane/siloxane emulsions with no more surfactant required. The particle size of the latex particles and the molecular weight of the PIBS was definable under effective temperature control and suitable concentration of surfactant. This would contribute to the film thickness during the application of the silane/siloxane emulsion on the concrete substrate (see Chapter 6). The use of PIBS latex enabled the possibility of preparing high siloxane content silane/siloxane emulsions with low viscosity. The presence of PIBS particles in the final silane/siloxane emulsion increased the water repellency of the treated concrete (see Chapter 6).

In order to assess the role of the PIBS in the final silane/siloxane emulsions it was necessary to investigate its properties. The investigation of the characteristics of the chosen PIBS latex in terms of viscosity, surface activity, zeta potential, particle size distribution, molecular weight distribution and stability was of importance to assess storage stability of the latex and storage stability of the PIBS latex/silane emulsions.

4.2. The mechanism of emulsion polymerisation of IBTMS

4.2.1. The hydrolysis and condensation of IBTMS monomer

In aqueous media, IBTMS hydrolyses to form isobutylsilanetriols (IBST):



Scheme 4.1. Hydrolysis of IBTMS

The freshly prepared solution of IBST is a clear solution in which IBST monomers and methanol are in an equilibrium state. Acids or bases may be used to catalyse the hydrolysis of alkylalkoxysilanes. According to Osterholtz and Pohl,[97] each change of pH by one pH unit in either acidic or basic direction will result in ten-fold acceleration in the hydrolysis rate and the anion of any acid may also further accelerate the hydrolysis of alkylalkoxysilanes. The hydrolysis of IBTMS has been found in this study to be accelerated in an acidic medium with an emulsifying agent, ABSA, as shown in Table 4.1. The use of ABSA as catalyst for the hydrolysis of IBTMS in this research has another advantage. ABSA is completely degraded in an aerobic environment.[98] Therefore the presence of ABSA in the final PIBS latex/silane emulsions would not have a long term effect on the water absorption of the treated concrete due to the surfactant wetting effect.

Concentration of ABSA (%w/w)	pH	Hydrolysis time (min.)
0.1	2.65	15
0.2	2.43	10
0.5	2.13	3
1.0	1.92	2
1.5	1.79	1

Table 4.1. Effect of ABSA on the relative rate of hydrolysis of IBTMS

(The ratio of IBTMS/H_2O was 2:3)

Osterholtz and Pohl[97] have demonstrated that at low pH, the hydrolysis of alkylalkoxysilanes occurs in steps and each step is related to the removal of one alkoxy group from the silane. The succeeding step of alkoxy removal is faster than the first and this is attributed to the relief of steric hindrance at silicon.[99] The mechanism for the acid-catalysed hydrolysis of IBTMS adapted from that proposed by Osterholtz and Pohl is shown in Figure 4.1. The hydrolysis of IBTMS in an acidic aqueous medium proceeds by rapid protonation of the methoxy group, followed by a bimolecular S_N2-type displacement of the leaving group by water. The rate of acid-catalysed hydrolysis of the alkylalkoxysilane depends on the alkoxy group of the silane.

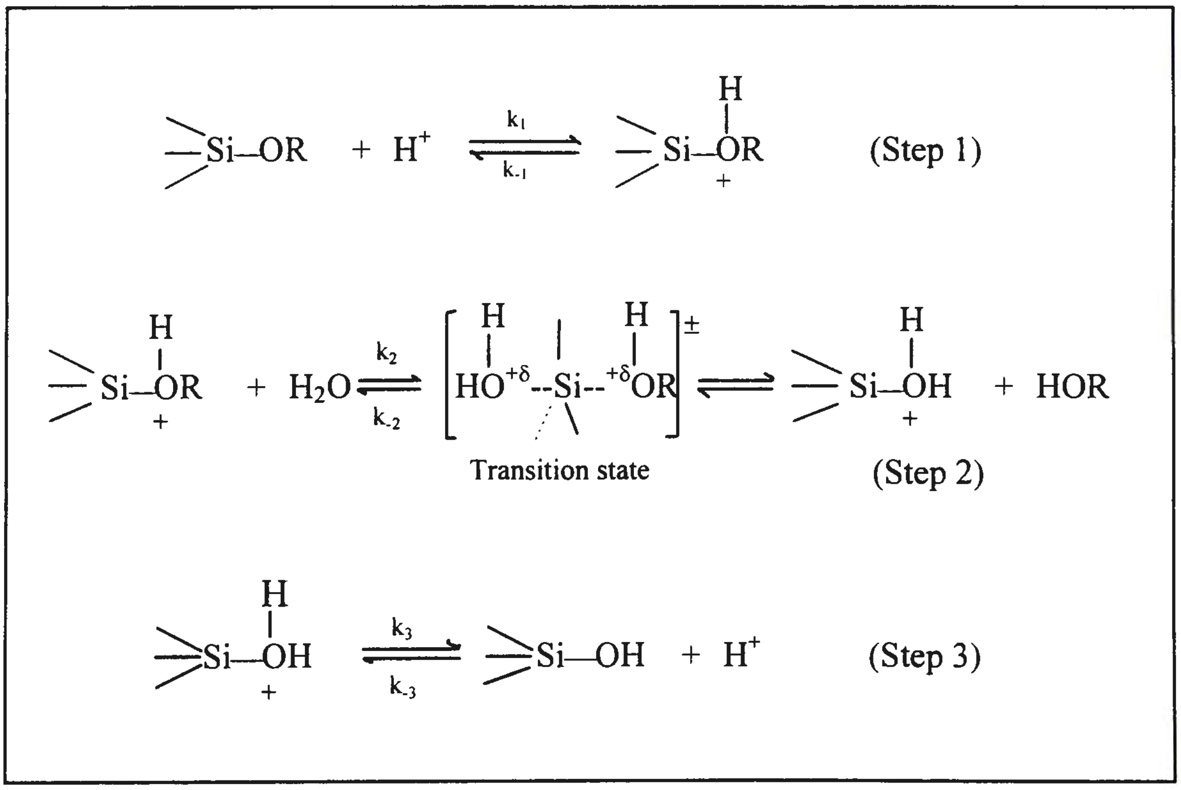


Figure 4.1. Proposed mechanism for the hydrolysis of an alkoxy group from IBTMS in acidic medium

As shown in Table 4.2, the rate of acid-catalysed hydrolysis of IBTMS is 6 times faster than that of isobutyltriethoxysilane (IBTES). This result is consistent with the work of Arkles et al.[100]

Alkylalkoxysilane	pH	Hydrolysis time (min.)
IBTMS	2.43	10
IBTES	2.43	60

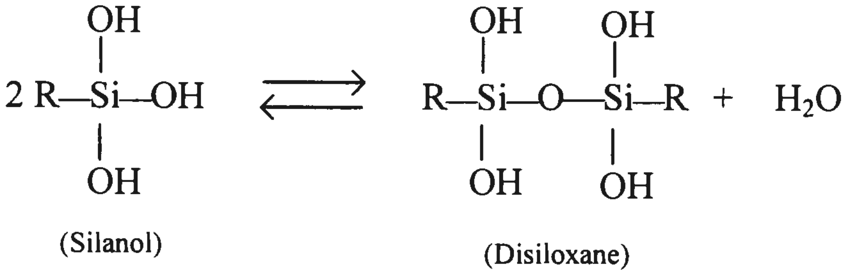
Table 4.2. The effect of the leaving group on the hydrolysis rate of isobutyltrialkoxysilanes in ABSA solution

The alkyl substituents on silicon also have an effect on the hydrolysis rate of alkylalkoxysilane under acidic conditions as shown in Table 4.3. Larger alkyl groups will retard the hydrolysis rate due to steric and inductive effects.

Alkylalkoxysilane	pH	Hydrolysis time (min.)
MTMS	2.43	3-4
IBTMS	2.43	10
OTMS	2.43	Very slow

Table 4.3. The effect of the alkyl group on the hydrolysis rate of alkyltrimethoxysilanes in ABSA solution

IBST monomers are intermediates in the hydrolysis reaction but they are not able to be isolated. In aqueous media, the condensation reactions of IBST approach equilibrium rather than completion as follows:



Scheme 4.2. Condensation reaction of IBST

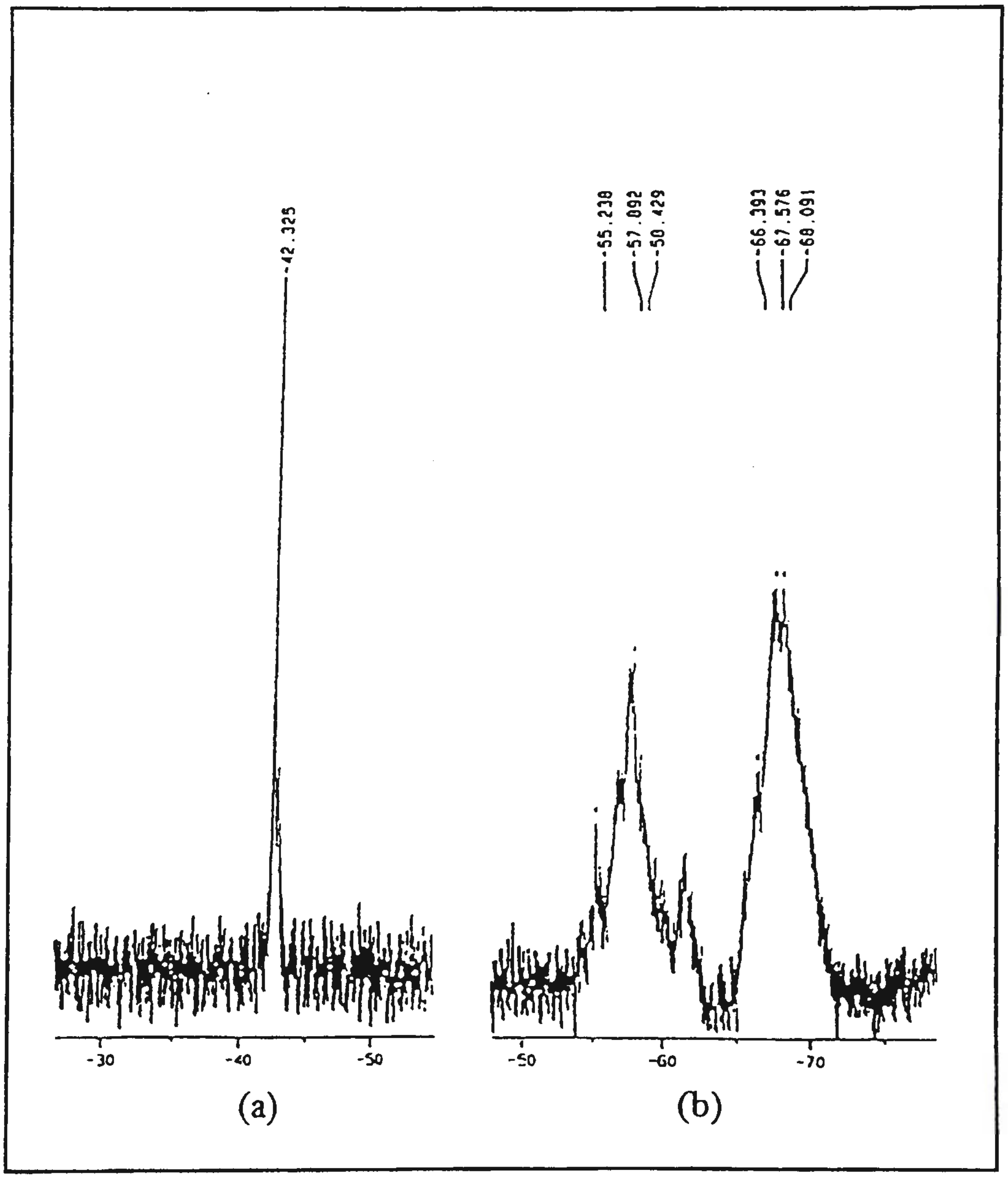
The equilibrium constant, K, is defined as:

$$K = \frac{[\text{Disiloxane}] \times [\text{H}_2\text{O}]}{[\text{Silanol}]^2}$$

Condensation of IBST is second order in silanol concentration. Therefore, doubling the concentration of silanol species multiplies the rate of formation of siloxane products four-fold. The condensation rate depends on the pH of the solution. According to Osterholtz and Pohl,[97] the minimum condensation rate for an alkylsilanol is obtained at approximately pH 4. In the study herein, the pH of the solution was maintained at between 3 and 4 to achieve a low rate of condensation by using a specific amount of SDBS for the emulsion polymerisation process.

Both the hydrolysis reactions and condensation reactions of alkylalkoxysilanes are reversible. The condensation of silanols proceeds more rapidly at higher temperatures. Therefore, the hydrolysis of IBTMS was undertaken at room temperature. Alcohol produced from the hydrolysis reaction stabilises the silanols in the solution. The removal of methanol from the IBTMS emulsion polymerisation process was undertaken slowly at a moderate temperature. The slow evaporation of methanol in the process and the maintenance of the pH between 3 and 4 prolongs the lifetime of the silanol monomers in the solution. This would allow the silanol monomers enough time to enter the SDBS micelles before they are condensed and reduce the number of silanol monomers undergoing condensation in the bulk solution. IBTMS was chosen as the silane monomer in the emulsion polymerisation reaction for several reasons. It is easily hydrolysed under acidic conditions compared to OTMS. The removal of methanol during the emulsion polymerisation of IBTMS can be carried out at a low temperature under atmospheric pressure. Further, the final product is a PIBS latex containing the isobutyl group as the alkyl group which contributes to the alkali stability after application of the PIBS latex/silane emulsion impregnants (as discussed in 6.5). Also the IBTMS is commercially available.

The polymer in the latex particles is a cross-linked polyisobutylsiloxane (PIBS) resin with terminal hydroxyl groups as shown in the ^{29}Si NMR spectrum of PIBS (Figure 4.2). In this figure, the sharp peak resonating at -42.32 ppm may be assigned to the Si atom of the IBTMS monomer. In the ^{29}Si NMR spectrum of PIBS, the broad peak resonating at about -57 ppm may be assigned to the silicon atom containing an hydroxyl group and the broad peak resonating at about -68 ppm may be assigned to the Si atom of the siloxane bond containing no hydroxyl group.



(a) (b)

Figure 4.2. ^{29}Si NMR spectra of (a) IBTMS and (b) PIBS

The ^{29}Si NMR assignment of IBTMS and PIBS is summarised in Table 4.4. These assignments are consistent with the work of Nishiyama and Horie[101] on the hydrolysis and condensation of γ-methacryloxypropyltrimethoxysilane and justified by the ^{29}Si CP/MAS chemical shift data of several kinds of Si compounds studied by Sindorf and Maciel.[102]

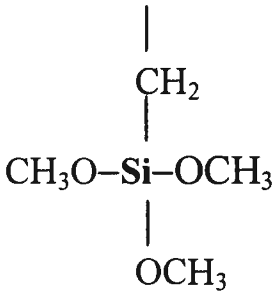
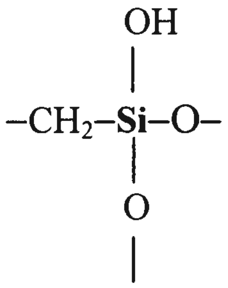
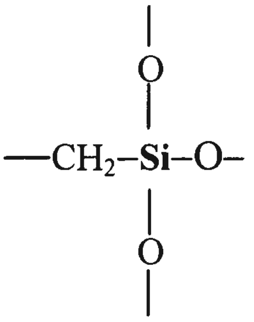
Assignment	δ (ppm)
 $\begin{array}{c} \vert \\ CH_2 \\ \vert \\ CH_3O-\mathbf{Si}-OCH_3 \\ \vert \\ OCH_3 \end{array}$	-42.325
 $\begin{array}{c} OH \\ \vert \\ -CH_2-\mathbf{Si}-O- \\ \vert \\ O \\ \vert \end{array}$	-57.892
 $\begin{array}{c} \vert \\ O \\ \vert \\ -CH_2-\mathbf{Si}-O- \\ \vert \\ O \\ \vert \end{array}$	-67.576

Table 4.4. Assignment of ^{29}Si NMR spectra of IBTMS and PIBS

4.2.2. The role of the surfactant in the emulsion polymerisation of IBTMS

In the emulsion polymerisation of IBTMS, the choice of surfactant is considered to be a very important factor. The surfactant must have the ability to stabilise polymer particles in the final polyisobutylsiloxane (PIBS) latex and not interfere adversely with the condensation of silanol monomer in the emulsion polymerisation process. Since the residual surfactant will remain in the final PIBS latex recovered after emulsion polymerisation, it must impart no adverse properties to the latex.

The major characteristic of a surfactant is that it appears at a higher concentration at the surface than in the bulk of a liquid and this phenomenon is known as adsorption. The adsorption of the surfactant at the surface is a consequence of its molecular structure. A surfactant contains both a hydrophilic and a hydrophobic group. The hydrophilic group makes the surfactant soluble in the aqueous phase whilst the hydrophobic group has only a slight affinity for water. In aqueous solution, the surfactant migrates to the water-air interface, resulting in a lowering of the surface tension of the water. If the external phase is organic, the hydrophobic portion of the surfactant is very compatible with the external phase and perhaps even soluble in it, and the tendency to migrate to the water-organic interface is increased. This results in a lowering of the interfacial tension between the water and organic phases. It is not likely that all the surfactant molecules will be adsorbed at the surface when the concentration of surfactant increases; the additional surfactant molecules remain in the bulk of the solution and their hydrophobic heads will still be expelled from the water. This expulsion is opposed by the hydrophilic groups and the end result is that the excess surfactant molecules aggregate together to form small colloidal clusters called micelles. The concentration of surfactant at which micelles start to form is called the critical micelle concentration (CMC). The CMC varies with different surfactants and its value is usually in the 0.08 to 0.30% range. In a dilute solution of 0.5 to 2.0% of surfactant, there is an equilibrium between micelles and single surfactant molecules in the aqueous phase. The number of single surfactant molecules in the aqueous phase depends on the CMC. According to McCoy,[103] surfactants with a low CMC give fewer single surfactant molecules than those with a high CMC. The CMC of surfactants in solution is related to the hydrocarbon chain of the molecule and can be defined in an empirical relationship[104] as follows:

$$\log_{10} CMC = \frac{\Delta G_m^{\ w}}{2.3RT} + n_c(\frac{\Delta G_m^{\ h}}{2.3RT}) + \log_{10} + \frac{K}{2.3RT} \tag{4.1}$$

where $\Delta G_m{}^h$ is the free energy term favouring micellisation, $\Delta G_m{}^w$ is the free energy term opposing micelle formation, K is a constant, and n_c is the number of carbon atoms in the hydrocarbon tail. Equation (4.1) shows that the CMC decreases as the number of carbons in the hydrophobic chain increases. In aqueous media, the CMC of ionic surfactants is approximately halved by the addition of each CH_2 group in their hydrocarbon chain.[105] The nature of the charged hydrophilic group of ionic surfactants has little effect on their CMC.[106]

Apart from the chemical constitution, the micellisation of a surfactant in an aqueous medium also depends on many other factors which can in turn influence the solubilising ability of the surfactant. It has been shown that the CMC of most ionic surfactants passes through a minimum as the temperature is varied from about 0°C to 70°C.[107] The addition of electrolytes such as alcohols, amines or mercaptans to the aqueous phase also causes the CMC to fall.[108] The size of the micelle is usually measured by the aggregation number which is the number of surfactant molecules going to make up the aggregate micelle. The size of micelles formed by non-ionic surfactants is very large compared to those from anionic or cationic surfactants.[106] Several different micelle structures are possible, but at relatively dilute concentration (1-2%) micelles are spherical[109] and are 20-100 nm in diameter.[110] Each micelle contains about 50-100 surfactant molecules.[111] In spherical micelles, the hydrocarbon ends of the surfactant molecules orient towards the interior of the micelle and their ionic ends orient outward, towards the water.

The use of SDBS in the emulsion polymerisation of IBTMS, has some advantages. Firstly, the size of the SDBS micelles is not very large compared to those from nonionic surfactants and this will not produce large polymer particles.

Secondly, the CMC of SDBS is relatively low due to its long hydrophobic carbon chain. Therefore, in aqueous media, the number of micelles is higher than the number of single surfactant molecules in the solution. Thirdly, SDBS is completely ionised in aqueous solution and the free sulphonic acid is water soluble so the solubility of SDBS is not affected[106] at low pH due to the presence of ABSA which was used as catalyst for the hydrolysis of IBTMS.

SDBS plays a significant role in the emulsion polymerisation process. It increases the amount of the silanol monomers taken into the water phase owing to solubilisation in micelles. It also emulsifies the silanol monomers into fine stable droplets. Once the polymerisation process has begun the SDBS protects the latex particles against coagulation during and after the emulsion polymerisation process. The number of SDBS micelles and their size depends on the amount of surfactant used compared to the amount of monomer. Larger amounts of surfactant will yield a larger number of small size micelles. The quantity of micellar SDBS also determines the number of polymer particles formed. The number of latex particles formed and the rate of the polymerisation reaction depends on the concentration of micellar surfactants.[111] When higher concentrations of SDBS are used, small latex particles are formed (ξ 4.2.2) but the residual surfactant remains in the PIBS latex and will have a wetting effect on the treated concrete on application of the final emulsion. If the concentration of SDBS is low, the amount of surfactant may be insufficient to cover and stabilise the ever growing surface of the latex particle. Consequently the latex is not stable and the addition of more surfactant is required for the production of stable PIBS latex/silane emulsions in the next process. The pH of the system depends on the concentration of SDBS. The pH of the system was maintained at 3-4 in order to control the rate of the condensation of silanol[112] and to assure the polycondensation of the silanol monomers mainly within the SDBS micelles.

4.2.3. The mechanism of the emulsion polymerisation process

Emulsion polymerisation of IBTMS is heterogeneous reaction and the mechanism of the process can be explained by the general theory of the mechanism of emulsion polymerisation developed by Harkins.[113]

In a dilute solution of SDBS above its CMC, SDBS micelles are formed. A small portion of the IBST monomer enters the interior hydrocarbon section of the micelles. This action is caused by the hydrophobic interaction between the tail of the surfactant molecule and the hydrocarbon group of the silanol monomers. A larger portion of the silanol monomer is dispersed as small droplets whose sizes depend on the intensity of agitation. These monomer droplets are stabilised in the water by the adsorption of surfactant molecules on the surface and they are quite a bit larger than the monomer swollen micelles. Under the effect of temperature and agitation, methanol slowly evaporates from the bulk solution. The condensation polymerisation of the IBST monomers takes place simultaneously and almost exclusively in the interior of the micelles as the methanol evaporates. The micelles are favoured as reaction sites[114] because of their high monomer concentration compared to the IBST monomer in the solution and their high surface-to-volume ratio compared to the IBST monomer droplets.

As polymerisation proceeds, the micelles grow by the addition of silanol monomer molecules from the aqueous phase whose monomer concentration is replenished by the diffusion of IBST monomer molecules from the IBST monomer droplets. The activated micelles become polymer particles with surfactant molecules adsorbed on their surface. As the polymer particles grow, the monomer droplets lose their IBST monomer and eventually disappear. A simplified schematic representation of the emulsion polymerisation system is shown in Figure 4.3. The separate parts of this figure relate to the various stages of the emulsion polymerisation system from initiation up to complete conversion.

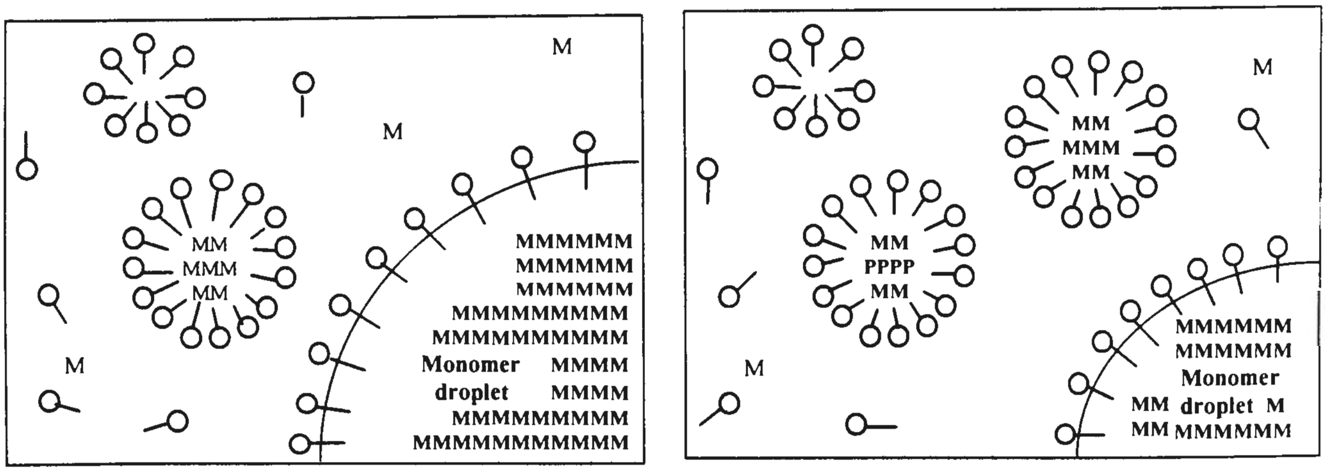
The system initially consists of three types of particles; namely silanol IBST monomer droplets, micelles free of IBST monomers, and micelles containing IBST monomers in which the condensation reaction is about to begin. At this stage, the surface free energy of the aqueous phase-air interface is low due to the adsorption of the surfactant molecules. The monomer droplets are very large relative to the micelles and they tend to coalesce if the system is not agitated.

At stage 1, the system is in the initial stages of the condensation reaction of silanol monomers. Some siloxane oligomers are now formed in the interior of the micelles.

At stage 2, all the silanol monomer-swollen micelles have disappeared. The number of surfactant molecules adsorbed on the monomer droplets has fallen, and so too has the amount of dissolved SDBS molecules. The size of the latent latex particles is increasing at the expense of silanol monomer droplets which have become smaller and fewer in number. The surface free energy of the aqueous phase-air interface has increased, the number of reaction loci is constant, and so too, therefore, is the polymerisation rate.

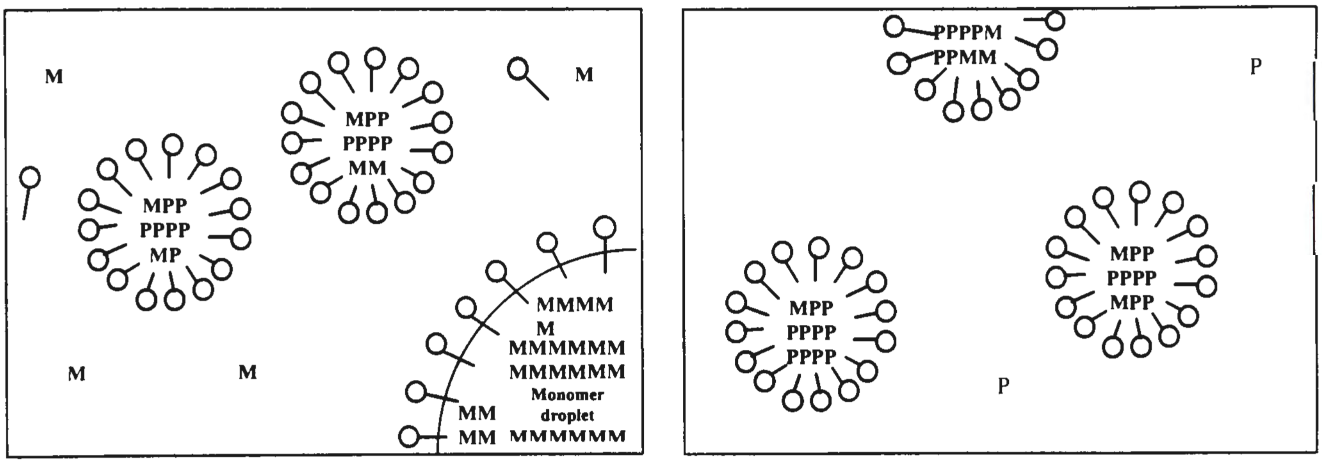
At stage 3, the silanol monomer droplets have disappeared and the system comprises polysiloxane particles which are dispersed in the aqueous phase and some “free” IBST monomers which later condense outside the micelles to form latex coagulum.

At the completion of the emulsion polymerisation process, the system comprises polyisobutylsiloxane (PIBS) particles which are dispersed in the aqueous phase. These PIBS particles are stabilised by the surfactant molecules of the original micelles. Latex coagulum is also present in the system therefore, the purification of the latex system is necessary.



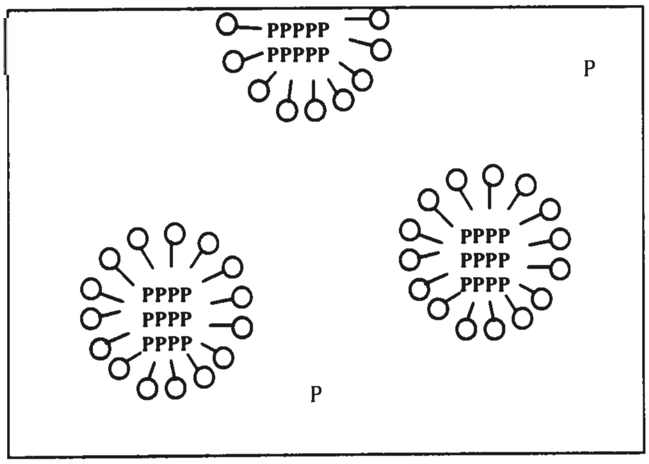
(a) Prior to condensation

(b) Stage 1, Shortly after condensation



(c) Stage 2, all the SDBS micelles consumed

(d) Stage 3, IBST monomer droplets disappear



O— represents an SDBS molecule

M represents a silanol monomer

P represents a PIBS molecule

(e) Stage 4, end of polymerisation

Figure 4.3. Schematic representation of stages of the emulsion polymerisation of IBTMS

Upon drying, the PIBS latex transforms from a milky, colloidal dispersion to a transparent, tough and continuous film. This indicates that the latex particles are soft spheres and further condensation between latex particles occurs upon drying. Investigation of the morphology of such a PIBS latex is very complex and time consuming. This was unable to be conducted in this research as a new method of preparing the surface replica for electron microscopic work was required.

The conversion of IBTMS to PIBS particles in the emulsion polymerisation process is time dependent. Higher conversion was achieved at longer reaction times as shown in Figure 4.4. A conversion yield of more than 80% was obtained after 12 hours reaction and slightly increased as the reaction time increased.

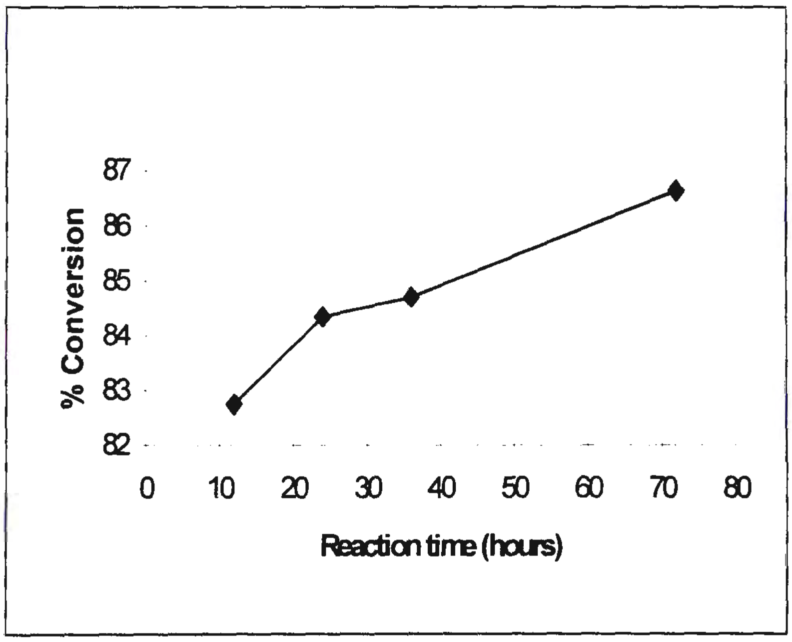


Figure 4.4. Effect of reaction time on percentage conversion of IBTMS

4.3. Characterisation of PIBS latex

4.3.1. Zeta potential of PIBS latex

The zeta potential of the PIBS latex is shown in Table 4.5. In this table, latex A had been stored at room temperature for more than one year. Latex B1 was freshly prepared and latex B2 was neutralised with morpholine. The results indicate that the polyisobutylsiloxane latex is an electrostatically stabilised system. The electrostatic charge at the surface of latex particles arises from the dissociation or protonation of the sulphonate group of the adsorbed surfactant on the surface of the particles. The layer of ionised surface groups and the diffuse ion atmosphere of compensating counter ions that surrounds each latex particle form the electrical double layer. Electrostatic repulsion between particles occurs when their electrical double layers overlap.

Sample	% Solids (w/w)	pH	Zeta potential (mV)
Latex A	30	4.6	-59.8
Latex B1	30	4.6	-60.2
Latex B2	30	7	-64.8

Table 4.5. Zeta potential of PIBS latex

Vergelati et al.[115] have studied the interfacial structure of silicone oil emulsions and the principles may be extended to the PIBS latex system. In the

PIBS latex, the OH end groups of the PIBS may concentrate at the surface of the latex particles as shown in Figure 4.5.

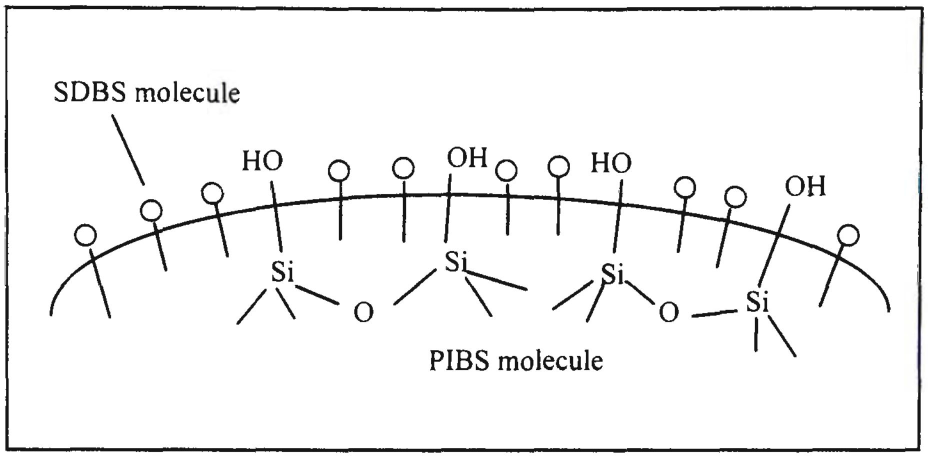


Figure 4.5. Schematic representation of mixed interfacial film of surfactants and the OH end groups of PIBS latex particles

The presence of the hydroxyl end group of PIBS at the surface may also contribute to the electrostatic repulsion between latex particles and leads to a high absolute value of the zeta potential of the PIBS latex.

The zeta potential of the PIBS latex which has been stored at room temperature for more than one year (latex A) and the freshly prepared latex (latex B1) were similar and this indicates that within the PIBS latex the magnitude of electrostatic repulsion forces was not changed during long term storage at room temperature. The zeta potential of the PIBS latex increased when it was neutralised with morpholine (the zeta potential of the latex B1 and the neutralised latex B2 are -60.2 mV and -64.8 mV respectively). This implies that some morpholine molecules may concentrate at the interface between polymer particles and the water phase and therefore the potential pattern changes.

4.3.2. Surface activity of PIBS latex

The surface tension of the PIBS latex at the water-air interface is shown in Table 4.6. Surface tension falls to the lowest value at a solids concentration of 30% and slightly increases as the solids concentration of the PIBS latex becomes greater than 30%. As the solids concentration increases up to 30%, the surface tension decreases as the number of polymer particles in the solution increases and thus the number of surfactant molecules adsorbed on polymer particle surfaces increases. At a solids concentration higher than 30%, the surface tension of the PIBS latex slightly increases and this may be attributed to the situation in the concentrated latex approaching the close packing of the PIBS particles in a layer.

Solids concentration (w/w)	Surface tension (dynes/cm)
10	37.77
20	34.69
30	31.90
40	32.29
50	34.02

Table 4.6. Surface tension of the PIBS latex at different concentrations

At a solids concentration of 30%, the surface tension of the PIBS latex decreased when the latex was neutralised with morpholine as shown in Table 4.7. The decrease in surface tension of the neutralised latex may be attributed to the surface activity of morpholine.

Solids concentration (w/w)	pH	Surface tension (dynes/cm)
30	4.6	34.4
30	7	32.0

Table 4.7. Surface tension of neutralised PIBS latex

4.3.3. Viscosity of PIBS latex

The viscosity of the PIBS latex was measured and a plot of apparent viscosity versus shear rate is shown in Figure 4.6. The viscosity of PIBS latex decreases with an increase in rate of shear and the latex exhibits shear thinning characteristics even at very low concentrations of solids. This shear thinning property may be attributed to the strong interactions between particles as a result of different effects.

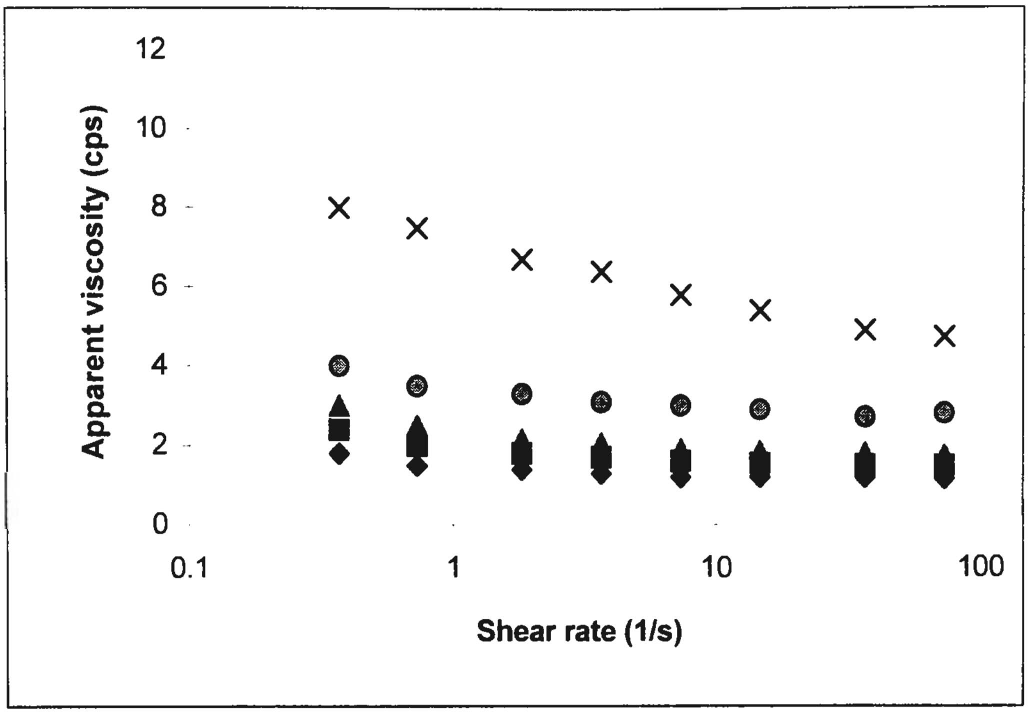


Figure 4.6. Apparent viscosity versus shear rate for PIBS latex at different concentrations of solids

(×) 50% solids ( ) 20% solids
(o) 40% solids (◊) 10% solids
(Δ) 30% solids

The viscosity of the PIBS latex is dependent on the concentration of solids. The change of viscosity with concentration is relatively small at a concentration of solids below 30% and very large between 30% and 50%. The increase in viscosity of the PIBS latex at a solids concentrations higher than 30% may be due to a combination of agglomeration of the polymer particles, and the effect of interparticle forces between polymer particles in a close-packed volume. At a solids concentration higher than 50%, the point of coagulation is approached. The changes in viscosity are greatest at low shear rates where the flow field has the smallest influence on distorting the electrical double layer and in which interparticle forces are dominant.[116]

Figure 4.7 represents the flow behaviour for the PIBS latex at five different concentrations of solids by measurement of shear stress-shear rate. The measurements of shear stress with change in shear rate show that PIBS latex is non-Newtonian with the flow being of the type generally referred to as plastic. The plasticity of the PIBS latex indicates that the latex has some inherent structure which completely resists shearing forces up to the magnitude τ_y, the so-called yield value, which is defined by the intercept of the flow curve with the shear stress axis.

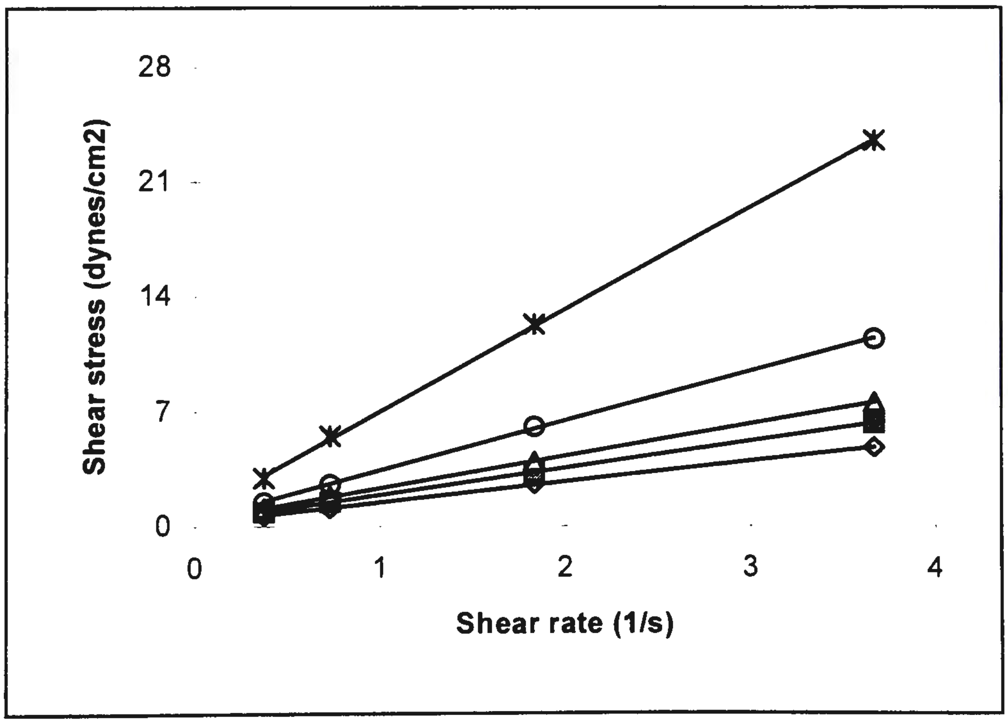


Figure 4.7. Flow behaviour of PIBS latex at different concentrations of solids

(×) 50% solids
( ) 20% solids
(o) 40% solids
(◊) 10% solids
(Δ) 30% solids

The yield values of the PIBS latex at different solids concentrations are shown in Table 4.8. As the yield value relates to the creaming ability of the latex[117], the results shown in Table 4.8 indicate that the creaming ability of the PIBS latex increases with the solids concentration.

Concentration of solids (% w/w)	Viscosity (cps)	Yield value (τ_y) (dynes/cm^2)
50	4.69	5.31
40	2.80	0.99
30	1.75	0.74
20	1.47	0.70
10	1.16	0.45

Table 4.8. Viscosities and yield values of PIBS latex at different concentrations of solids

4.3.4. Molecular weight distribution of PIBS latex

Figure 4.8 shows the molecular weight distribution (MWD) of the PIBS latex as determined by gel permeation chromatography (GPC). The average molecular weight of the PIBS latex is in the range between 1,000 and 4,000. The MWD of the latex exhibits bimodal character and is relatively narrow. The MWD of the PIBS latex is independent of the reaction time as shown in Figure 4.9.

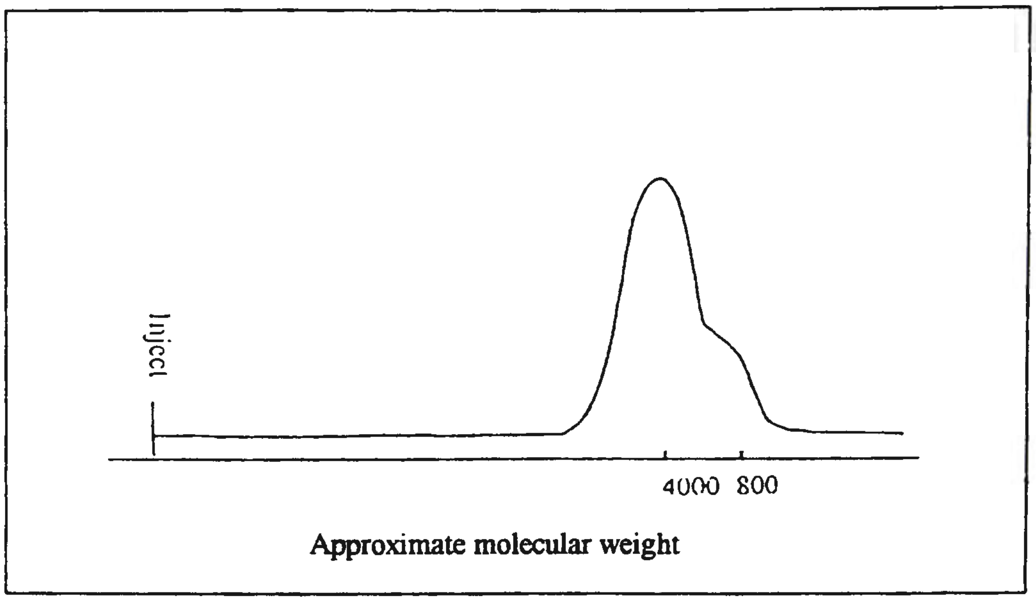


Figure 4.8. Molecular weight distribution of PIBS latex

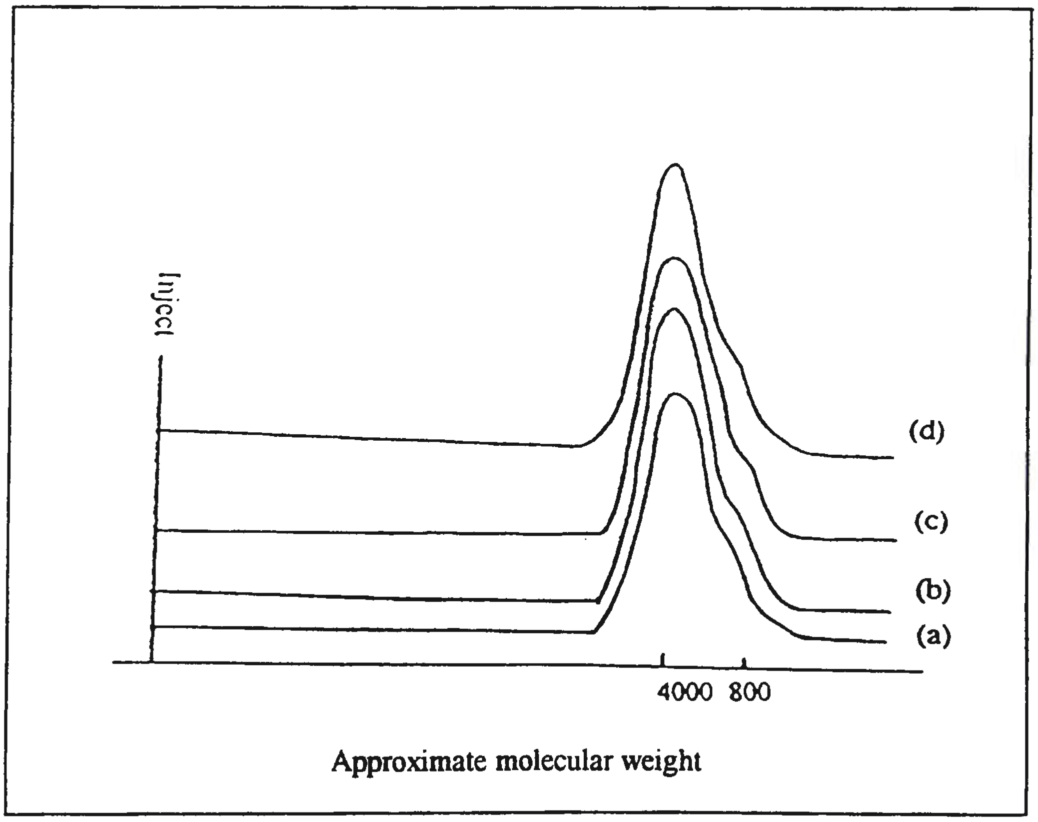


Figure 4.9. Effect of reaction time on the molecular weight distribution of PIBS latex

(a): 12 hours; (b): 24 hours; (c):36 hours; and (d): 72 hours

The SDBS concentration also has an effect on the MWD of the PIBS latex (Figure 4.10). The average molecular weight decreases with the increase in surfactant concentration. This implies that the number of SDBS micelles and the size of the micelle has a significant influence on the MWD of the PIBS latex.

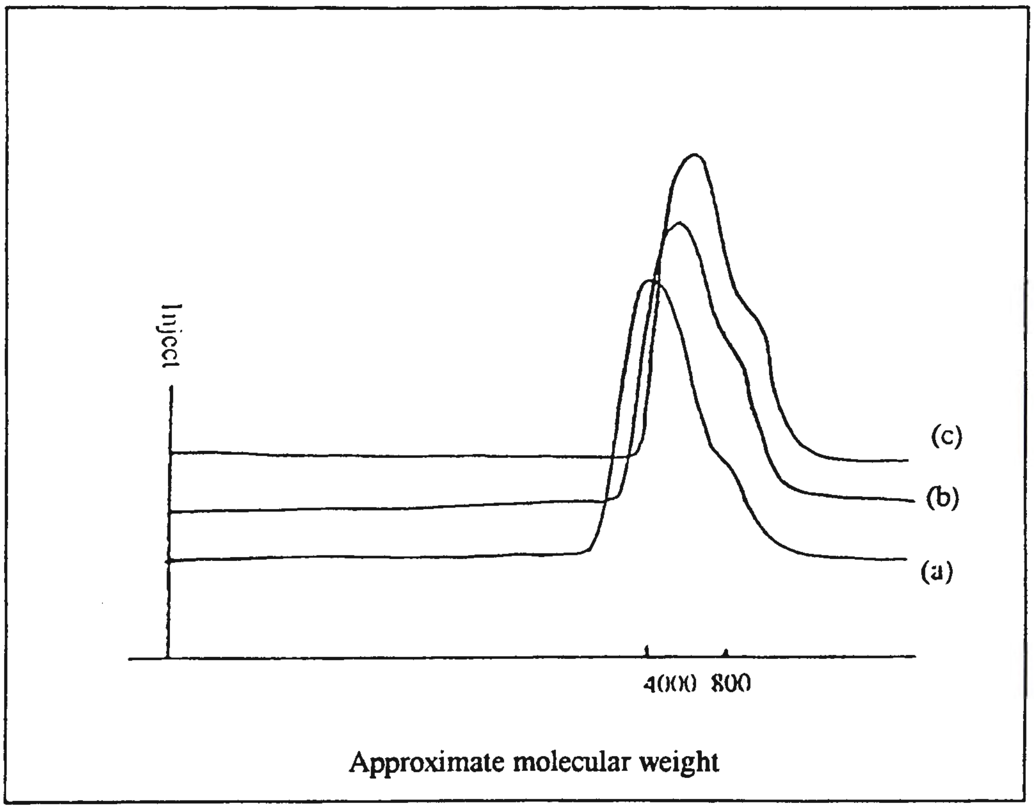


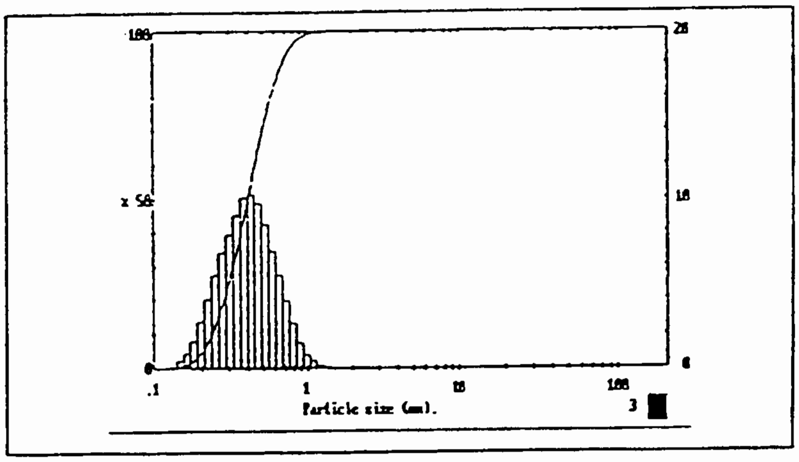
Figure 4.10. Effect of surfactant concentration on the molecular weight distribution of PIBS latex (a) 2% SDBS; (b) 3% SDBS; (c) 4% SDBS

Since the small particle size latex depends on the ability of the surfactant to stabilise the particles once they are formed, the result indicates that SDBS is a good stabiliser for the emulsion polymerisation of IBTMS. SDBS has the ability to form small PIBS particles and prevents them agglomerating into large particles (physical effect).

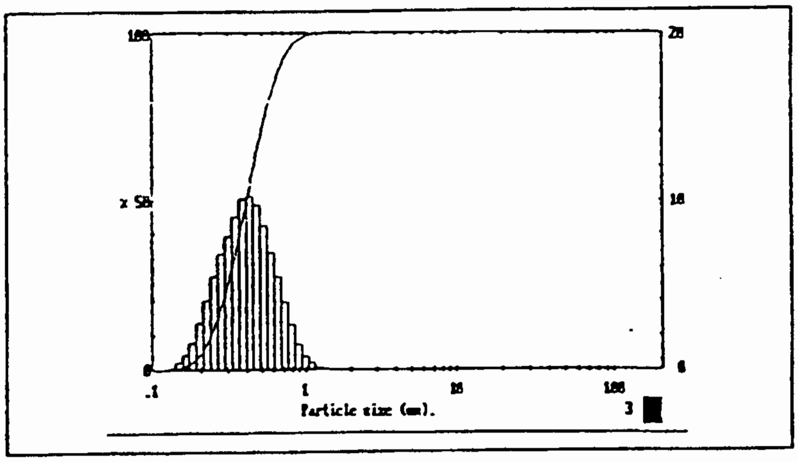
4.3.5. Particle size distribution of PIBS latex

The particle size distribution (PSD) of the PIBS latex is shown in Figure 4.11. The PSD curve shows that the PIBS latex is a polydispersed system containing different particles ranging from small particles of 0.1 micron to some large particles of more than 1 micron. The PSD of the PIBS latex does not change during storage.

The distribution of particle size becomes narrower and the average particle size decreases with an increase in the surfactant concentration (Figure 4.12). This implies that the concentration of the surfactant has an effect on the monodispersity of the system. As the concentration of the surfactant increases, the number of SDBS micelles and thus the number of reaction sites increases. Consequently, the size of the latex particles decreases as the number of reaction sites increases. The change in the number of latex particles with surfactant concentration is shown in Table 4.9. The number of latex particles per unit volume (specific surface area) increases as the concentration of the SDBS increases.



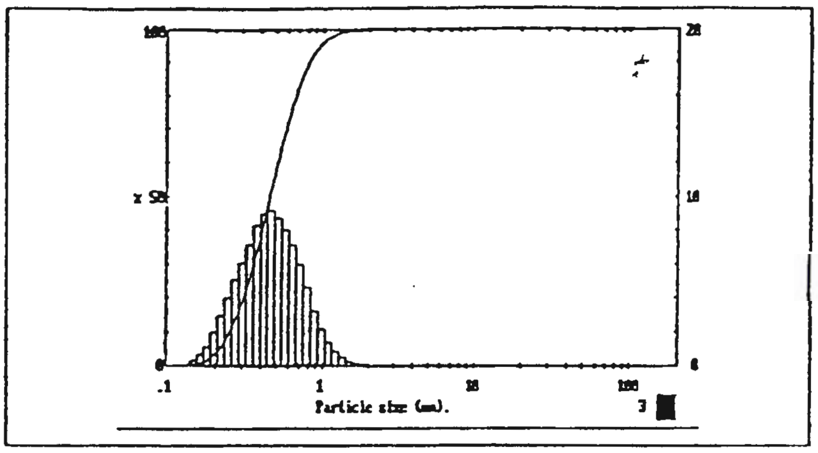
(a) freshly prepared latex



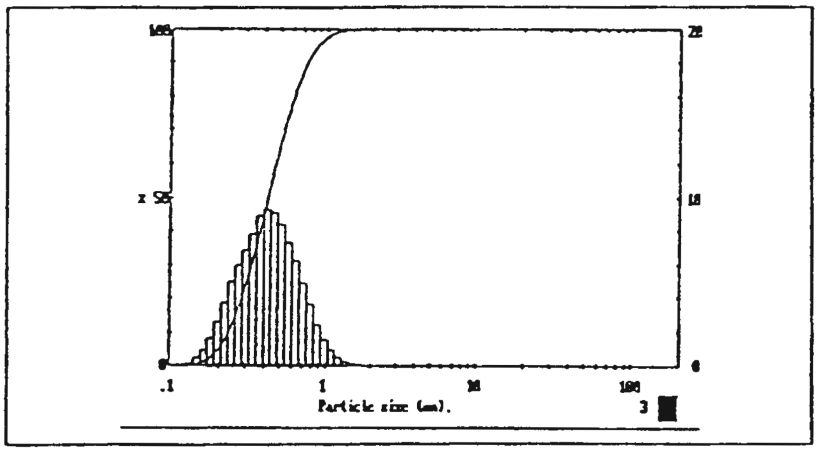
(b) one year old latex

Figure 4.11. Particle size distribution of the PIBS latex

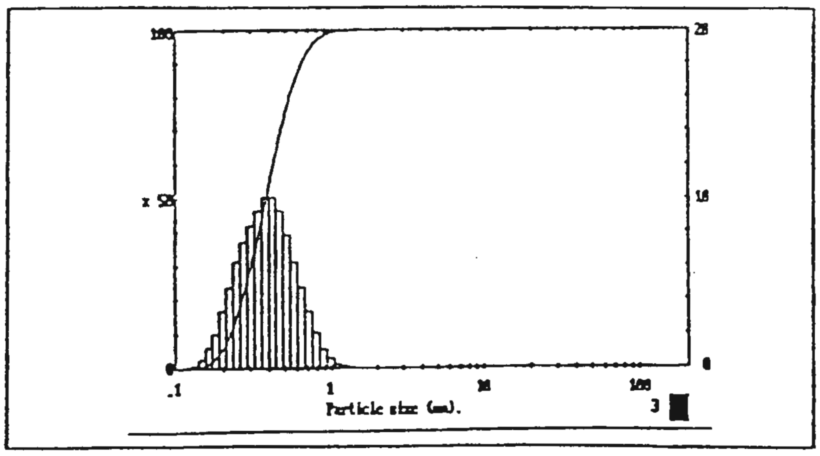
The result also indicates that the SDBS micelles are reaction sites for the emulsion polymerisation of IBTMS as the particle sizes of the polymer particles depends on the number of SDBS micelles.



(a) 2% SDBS



(b) 3% SDBS



(c) 4% SDBS

Figure 4.12. Effect of the concentration of surfactant on the particle size distribution of the PIBS latex

Surfactant concentration (%w/w)	Specific surface area (m^2/ml)
2	16.0580
3	16.4143
4	21.7448

Table 4.9. Effect of surfactant concentration on the specific surface area of the PIBS latex

4.4. The stability of PIBS latex

The PIBS latex is a colloidal solution and its stability is governed by the same principles as colloidal sols in general. There are several factors which may contribute to the stability of the PIBS latex . These factors are: (a) the particle size of the PIBS latex exhibits a relatively narrow distribution in the range between 0.01 to 1.00 microns; (b) the PIBS latex exhibits a yield stress at a low level of shear; (c) the zeta potential of the latex is relatively high at more than -50 mV.

According to Shaw,[118] larger particles are less stable than smaller particles on account of their smaller area-to-volume ratio, and so will tend to grow at the expense of the small particles. If this process continues, the latex will eventually break. The particle size distribution of the PIBS latex is relatively narrow and this indicates that the latex has a fairly uniform droplet size, and therefore the PIBS latex is less prone to this effect.

The PIBS latex exhibits a strong yield stress and a shear thinning behaviour. This implies that the latex is stabilised by strong electrostatic forces of repulsion.[119] The strong electrostatic forces of repulsion between the particles in the PIBS latex is also shown by the relatively high zeta potential of the latex. The absolute value of the zeta potential of the PIBS latex is about 60 mV and this is higher than the minimum value of 30 mV required for a stable emulsion.[120] The electrostatic repulsion arising from the charged double layer around the latex particle effectively decreases the van der Waals attractive forces between the latex particles. Hence, this prevents the close approach of the particles and prevents subsequent coalescence.

Another factor which may contribute to the stability of the PIBS latex is the presence of the hydroxyl end groups of the PIBS at the water-oil interface. In latex particles, the polymer is a cross-linked polysiloxane with hydroxyl end groups. The presence of the hydroxyl groups at the oil-water interface leads to the perturbation of the interfacial energy (ξ 4.3.1). As a result, the PIBS has a peculiar surfactant behaviour. The closed-packed interfacial film composed of surfactants and hydroxyl groups at the oil-water interface would possess greater strength and resistance to rupture. Hence, the particles would be less liable to coalesce and the latex achieves significant stability. This physical barrier around the particles also increase the height of the energy barrier V_{max} (see Chapter 2) and thus contributes to the stability of the latex. In conclusion, the stability of the PIBS latex may be attributed to the strong electrostatic repulsion of the adsorbed ionic emulsifier which is supplemented by the presence of the hydroxyl groups of the polyisobutylsiloxane.

At low concentration of solids, the latex particles are not close together and the attraction is overcome by the repulsion between particles and the interparticle forces are strong enough to prevent coalescence. As the concentration of solids increases, the distance between particles becomes smaller, the attraction forces overcome the electrostatic repulsion forces, leading to the aggregation or coagulation of the latex particles and the latex becomes unstable. For this reason, the PIBS latex should be stored as a concentrate which contains less than 50% of solids.

CHAPTER FIVE

Characterisation and stability of novel silane/siloxane emulsions

5.1. Characterisation of novel silane/siloxane emulsions

As discussed previously, the required properties of the silane/siloxane emulsions are deep penetration, alkali stability, physical stability, chemical stability, good beading effect (no wetting effect due to surfactant) and good performance in terms of water absorption.

In addition, ideally the emulsion should be preparable at a high concentration of silane and be dilutable to 20-25%. In the diluted state, it is necessary for the emulsion to exhibit satisfactory viscosity to spread on the substrate surfaces by normal application.

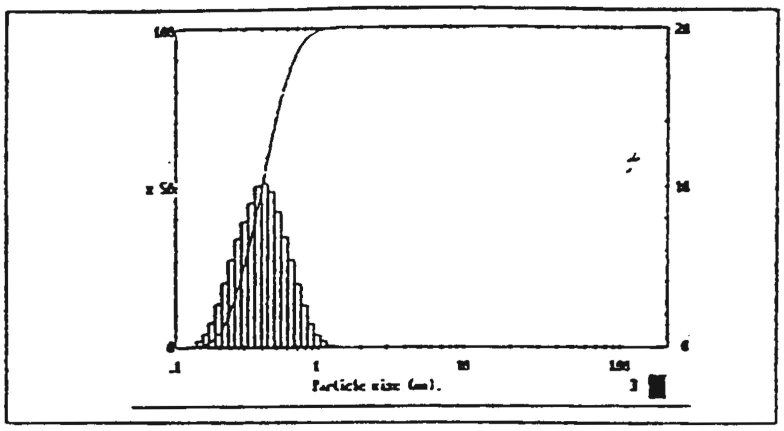
The stability of an emulsion is governed by its physical properties which determine its characteristics and usefulness for intended applications. Therefore, in this Chapter, the various properties such as particle size, particle size distribution, viscosity, zeta potential and the stability of the alkylalkoxysilane in the novel emulsions will be discussed. The stability of the novel silane/siloxane emulsions will be discussed in the last section of this Chapter.

5.1.1. Particle size distribution of novel silane/siloxane emulsions

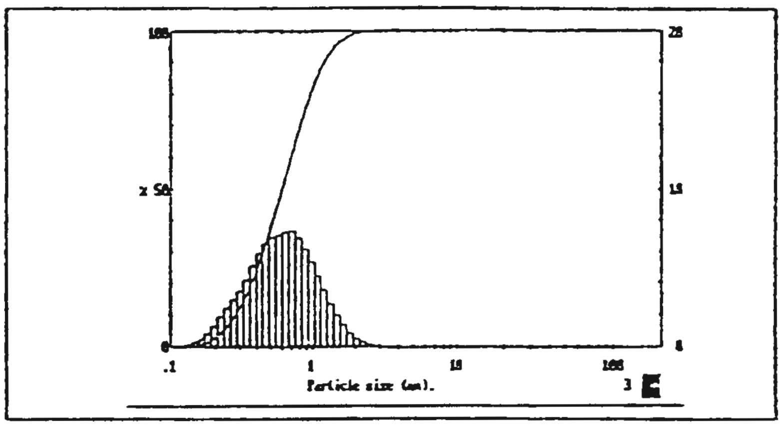
5.1.1.1. Particle size distribution of PIBS latex/silane emulsions

The particle size distribution (PSD) of the PIBS latex/silane emulsions is broader than the PSD of the PIBS latex itself as shown in Figure 5.1. The result shows that when silane is added to the PIBS latex, the PSD of the PIBS latex is shifted to a larger size distribution, resulting from the formation of larger silane droplets in the emulsion (Figure 5.1a and 5.1b). Therefore, the number of particles per unit volume (specific surface area) of the emulsion is smaller than that of the latex (Table 5.1).

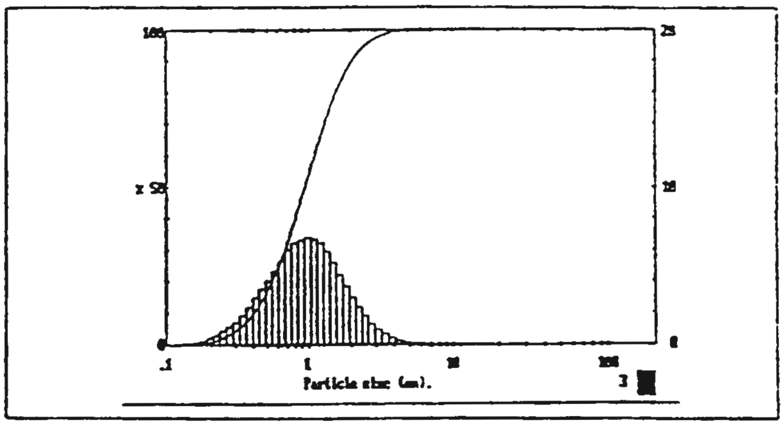
Table 5.1 shows that the specific surface area (SSA) of the PIBS latex/ OTES emulsion is lower than that of the PIBS latex/IBTES emulsion. The molecular size of OTES is larger than the molecular size of IBTES due to the hydrocarbon chain of the octyl group in OTES being longer than the hydrocarbon chain of the isobutyl group in IBTES. Therefore, the oil droplets in the OTES emulsion may be larger than the oil droplets in the IBTES emulsion. As a result, the number of particles per unit volume of the PIBS latex/OTES emulsion is lower than that of the PIBS latex/IBTES emulsion.



(a) PIBS latex (mean diameter = 0.40 µm)



(b) PIBS latex/IBTES emulsion (mean diameter = 0.71 µm)



(c) PIBS latex/OTES emulsion (mean diameter = 1.08 µm)

Figure 5.1. Particle size distributions of PIBS latex and PIBS latex/silane emulsions

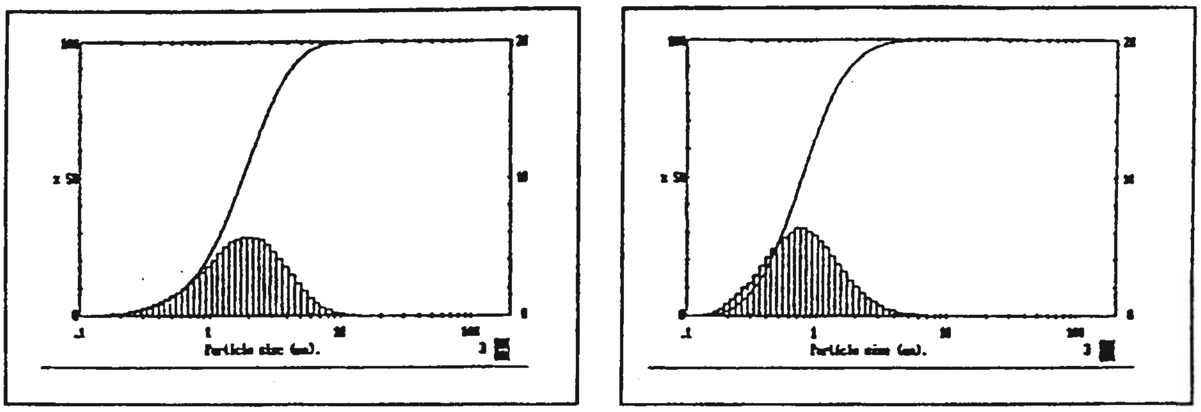
Emulsion type	SSA (m^2/ml)
PIBS latex	16.0580
PIBS latex/IBTES emulsion	12.8165
PIBS latex/OTES emulsion	7.9357

Table 5.1. Specific surface area of the PIBS latex containing 30% solids and PIBS latex/silane emulsions containing 18% solids

a. Effect of solids concentration on PSD of PIBS latex/silane emulsions

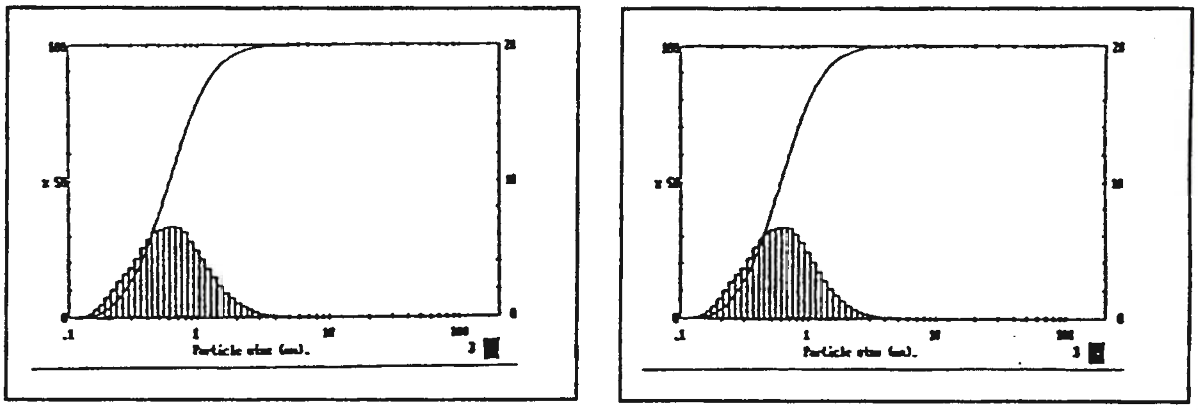
The effect of the concentration of solid particles (PIBS) on the PSD of PIBS latex/silane emulsion containing 40% of silane was studied at different concentrations of PIBS latex.

The results show that the solids concentration of the PIBS latex has a marked effect on the PSD of the PIBS latex/silane emulsions (Figure 5.2). As the solids concentration of the latex increases, the PSD of the emulsion becomes narrower and the SSA of the emulsion increases (Table 5.2). At 18% solids concentration, the emulsion has the highest SSA. The SSA of the emulsion decreases at solids concentration of the latex higher than 18% by weight. When silane is added to the latex with high speed mixing, silane droplets are formed in the system. The size of the silane droplets decreases as the solids concentration due to the latex increases and the PSD of the emulsion becomes narrower. The SSA of the emulsion increases as a result of the increase in the number of particles per unit volume.



(mean diameter = 2.13 µm)
(a) 6% solids

(mean diameter = 0.93 µm)
(b) 12% solids



(mean diameter = 0.71 µm)
(c) 18% solids

(mean diameter = 0.70 µm)
(d) 24% solids

Figure 5.2. Effect of solids concentration on the PSD of the PIBS latex/IBTES emulsion

At a solids concentration of the latex higher than 18% by weight, coagulation of the PIBS particles may occur. Large particles tend to grow at the expense of the small particles as the small particles are forced close together and the collisions between them occur more frequently. This results in a lowering of the area-to-volume ratio and thus the SSA of the emulsion.

Solids concentration (%w/w)	SSA (m^2/ml)
6	4.7914
12	9.6054
18	12.8165
24	12.0090

Table 5.2. Effect of solids concentration on the specific surface area of the PIBS latex/IBTES emulsion

b. Effect of silane concentration on PSD of PIBS latex/silane emulsions

Figure 5.3 shows the relationship between silane concentration and the SSA of the emulsion. The SSA of the emulsion increases with the increase in silane concentration up to 40%. The SSA of the emulsion then decreases as the silane concentration rises above 40%. A low concentration of silane results in a small number of silane droplets formed in the emulsion. Therefore the SSA of the emulsion is lower. At concentrations of 40% silane, the SSA of the emulsion reaches a maximum value. The SSA of the emulsion containing 50% silane is lower than that of the emulsion containing 10% silane. This may be attributed to the formation of larger silane droplets in the emulsion containing more than 40% silane. Therefore, when the solids concentration of the emulsion remains constant, extra silane added to the emulsion will result in an increase in silane droplets in the emulsion. The interparticle attractions between silane droplets becomes stronger as the collisions between them become more frequent. Coalescence of the silane droplets then occurs and larger silane droplets are formed.

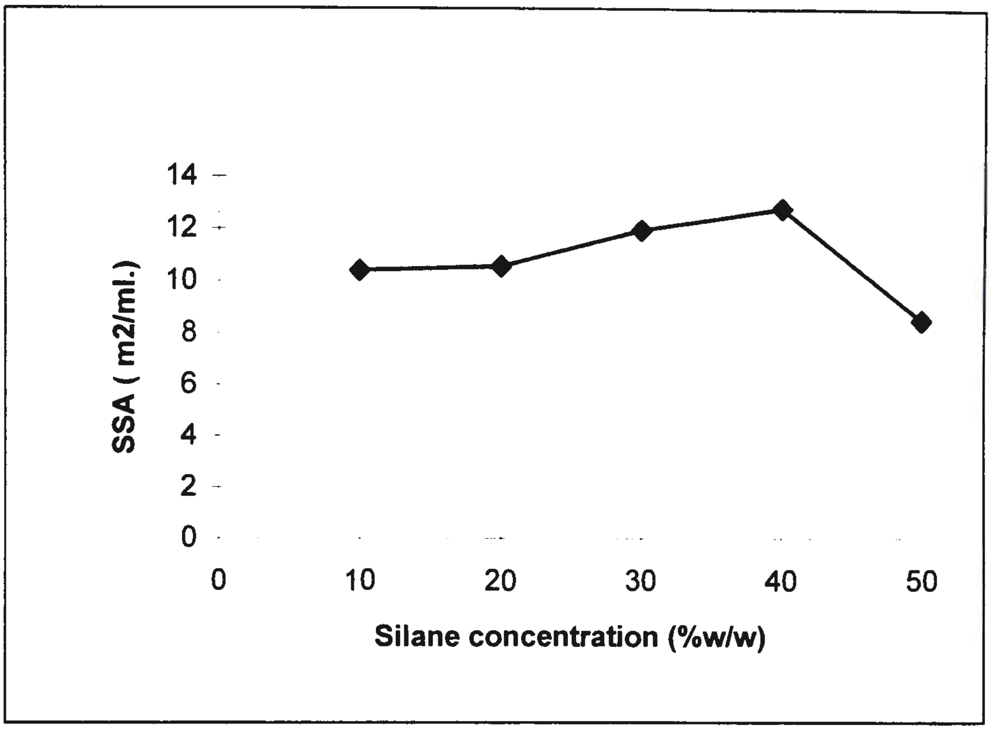


Figure 5.3. Relationship between SSA and silane concentration

The formation of larger droplets in emulsions containing more than 40% silane contributes to the instability of the emulsions. In support of this explanation, it has been found that the shelf life of the PIBS latex/silane emulsions containing 50% silane was less than one week.

c. Effect of shearing on PSD of PIBS latex/silane emulsions

The effect of shearing time by the shear mixer on the SSA is shown in Figure 5.4. The SSA of the emulsion increases with an increase in the shearing time.

The SSA of the emulsion reaches a maximum value at 20 minutes of shearing. Thereafter, the SSA decreases as the shearing time increases.

According to Gopal,[121] emulsification is a balance between disruption and recombination process. In the first few seconds of shearing, the disruption is dominant in the emulsification process. The bulk liquid is shattered into droplets. At this stage, only a small number of silane droplets are present and the coalescence of the droplets has not occurred. As the time of shearing increases, the number of silane droplets increases and the collisions among them become more frequent. After a certain time of shearing, the coalescence of the droplets reduces the number of particles in the emulsion. The limiting value of the SSA of the emulsion is reached at this time. This value is governed by the balance between disruption and recombination.

In PIBS latex/silane emulsions, the recombination of the particles becomes dominant in the emulsification process after 20 minutes shearing. At this time, the coalescence of the particles occurs as a result of mutual collisions among the particles. Therefore, the number of particles in the emulsion decreases. Consequently, the SSA of the emulsion decreases at shearing times greater than 20 minutes.

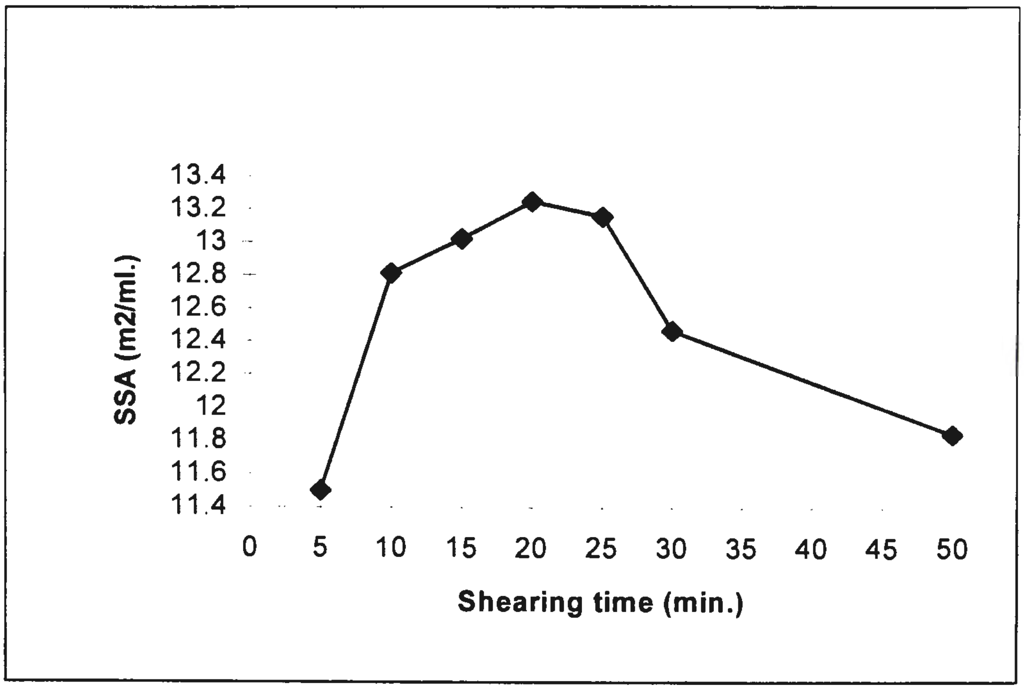


Figure 5.4. Effect of shearing time on the SSA of the PIBS latex/IBTES emulsion

The speed of the shear mixer also has an effect on the SSA of the emulsion as shown in Figure 5.5. The SSA of the emulsion increases with an increase in the speed of the shear mixer. The maximum value of the SSA is reached at a speed of 20,500 rpm. Thereafter, the SSA of the emulsion decreases as the speed of the shear mixer increases.

These results are consistent with the previous reported results of several workers.[122,123,124,125] They found that the SSA of an emulsion increases with an increase in the rotational speed and an increase in the diameter of the stirrer, and with a decrease in the diameter of the container tank.

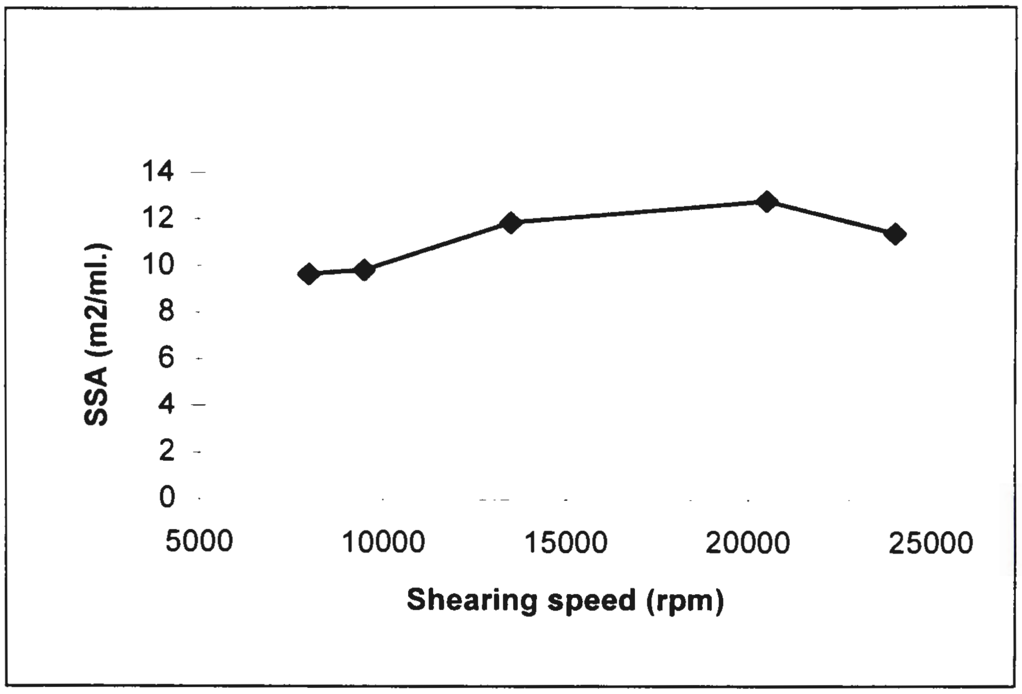
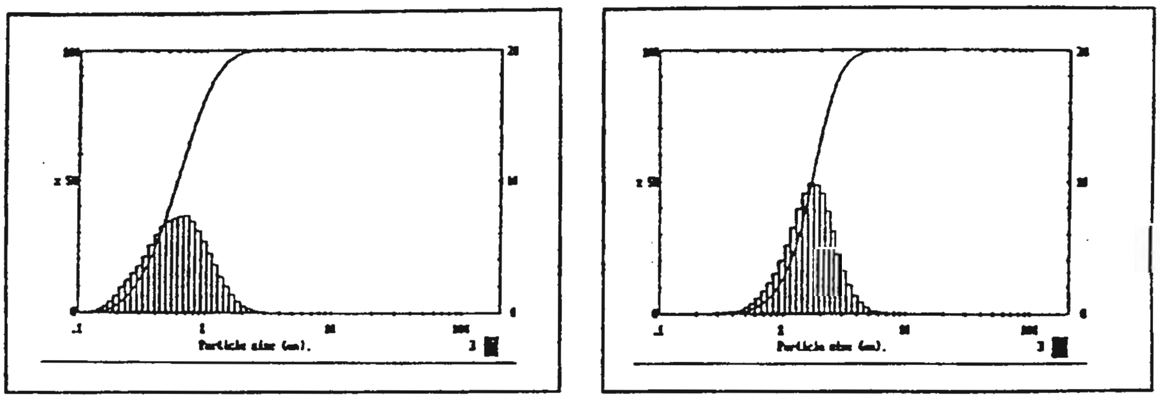


Figure 5.5. Effect of shearing speed on the SSA of the PIBS latex/IBTES emulsion

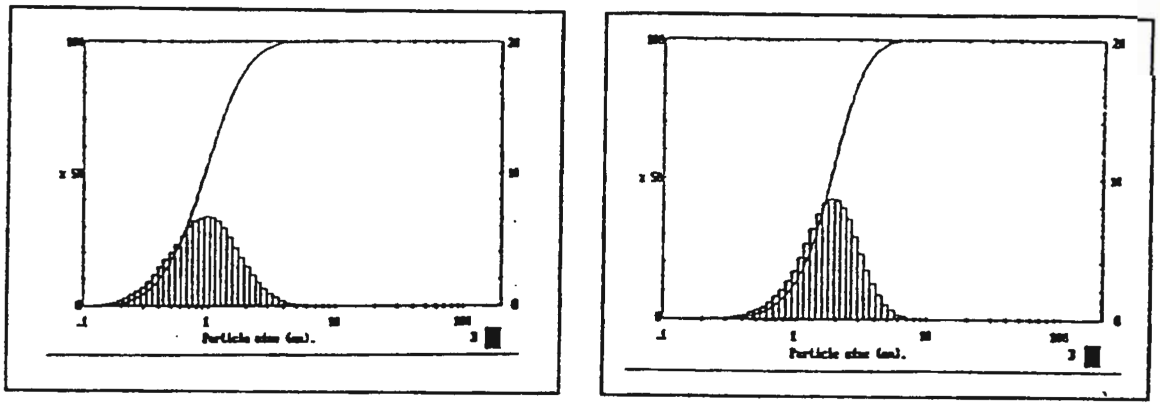
5.1.1.2. Particle size distribution of PDMS/silane emulsions

Particle size analysis of the emulsions produced from PDMS/alkylalkoxysilane mixtures shows that the particle size distribution (PSD) of the PDMS/silane emulsions is narrower than that of the PIBS latex/silane emulsions but in a range larger in particle size (Figure 5.6). The results show that the size of the oil droplets in the PDMS/silane emulsions are much larger than the size of the oil droplets in PIBS latex/silane emulsions. The PSD of the PDMS/silane emulsion is relatively narrower than that of the PIBS latex/silane emulsion. This indicates that the monodispersity of the PDMS/silane emulsions is higher than that of the PIBS latex/silane emulsions.



(mean diameter = 0.71 μm)
(a) PIBS latex/IBTES emulsion

(mean diameter = 1.79 μm)
(b) PDMS/IBTES emulsion



(mean diameter = 1.08 μm)
(c) PIBS latex/OTES emulsion

(mean diameter = 1.97 μm)
(d) PDMS/OTES emulsion

Figure 5.6. Particle size distribution of the PIBS latex/silane emulsions and PDMS/silane emulsions

Table 5.3 shows that the SSA of PDMS/silane emulsions is lower than that of PIBS latex/emulsions. This may be attributed to the presence of large oil droplets in PDMS/silane emulsions. The present of large oil droplets in the emulsions reduces the number of particles per unit volume. Therefore, the SSA of the PDMS/silane emulsions is lower than those of the PIBS latex/silane emulsions.

Emulsion type	SSA (m^2/ml)
PIBS latex/IBTES emulsion	12.8165
PIBS latex/OTES emulsion	7.9357
PDMS/IBTES emulsion	3.9250
PDMS/OTES emulsion	3.0827

Table 5.3. SSA of the novel silane/siloxane emulsions

The concentration of the amine soap also has an effect on the size of the oil droplets in PDMS/silane emulsions (Table 5.4). The mean diameter of the oil droplets in the PDMS/IBTES emulsion decreases as the concentration of amine soap increases. As a result, the number of particles per unit volume and thus the SSA of the emulsion increases in relation to the amine soap concentration.

Amine soap concentration (% by weight)	Mean diameter of oil droplets (μm)	SSA ($m^2/ml.$)
0.5	2.18	3.5825
1.0	1.79	3.9250
1.5	1.67	5.1122
2.0	1.58	5.9271

Table 5.4. Effect of amine soap concentration on the mean diameter of the oil droplets in PDMS/IBTES emulsion

(The emulsion contained 40% IBTES, 10% PDMS and was prepared at 24,500 rpm)

5.1.2. Zeta potential of novel silane/siloxane emulsions

The zeta potentials of PIBS latex/silane and PDMS/silane emulsions are shown in Table 5.5. These results show that the absolute value of the zeta potentials of the OTES emulsions is lower than that of the IBTES emulsions. There is little difference in zeta potential value between PIBS latex/IBTES emulsion and PDMS/IBTES emulsion (-57.2 mV and -56.4 mV respectively). The absolute value of the zeta potentials of the novel emulsions are relatively high compared to the absolute critical zeta potential value of 30 mV.[120] Therefore, the zeta potential may be the most important factor affecting the stability of the novel emulsions. A higher absolute value of the zeta potential results in a strong electrostatic repulsion between particles in the emulsion which prevents the close approach of the particles and subsequent coalescence.

The results also show that the addition of silane into the PIBS latex lowers the absolute value of the zeta potential of the system. The lower absolute zeta potential value of the PIBS latex/silane emulsions compared to the PIBS latex may be attributed to the reduced interaction of the electrical double layers around the emulsion particles. When silane is added to the latex, silane droplets are formed in the system with the aid of the residual "free" surfactant in the PIBS latex. In the PIBS latex/silane emulsion, the latex particles are sandwiched between silane droplets. The addition of the silane to the latex reduces the number of particles per unit volume and thus the interaction between particles becomes weaker. The electrostatic repulsion between latex particles in the PIBS latex/silane emulsion decreases since the presence of the silane droplets makes the electrical double layer around the latex particles interact less.

Sample	Zeta potential (mV)
PIBS latex/IBTES emulsion	-57.2
PIBS latex/OTES emulsion	-44.9
PDMS/IBTES emulsion	-56.4
PDMS/OTES emulsion	-40.5

Table 5.5. Zeta potentials of the novel silane/siloxane emulsions

The significantly lower absolute value of the zeta potential of the OTES emulsions compared to the IBTES emulsions may be attributed to the large size of the OTES droplets. The large size of the OTES droplets results in a small number of particles per unit volume. The distance between particles increases, the electrical double layers around particles interact less and the electrostatic repulsion between particles becomes weaker. This results in a lower zeta potential value of the OTES emulsions compared to the IBTES emulsions.

In the PDMS/silane emulsions, the electrostatic repulsion between oil droplets arises from the adsorption of the anionic surfactant at the oil/water interface, resulting in the formation of the electrical double layer around the emulsion droplets. The absolute value of the zeta potentials of the PIBS latex/silane emulsions are higher than the corresponding PDMS/silane emulsions. This indicates that the electrostatic repulsions between oil droplets in PDMS/silane emulsions are weaker than the electrostatic repulsions between particles in the PIBS latex/silane emulsions.

5.1.3. Viscosity of novel silane/siloxane emulsions

5.1.3.1. Viscosity of PIBS latex/silane emulsions

Viscosity is considered to be an important factor in the application properties of the emulsion. Emulsions with very low viscosity will cause difficulties in forming a liquid film on vertical surfaces in the impregnation process.

It is necessary for the silane/siloxane emulsion to have a suitable viscosity which not only holds the emulsion on the vertical surface but also allows it to break so that the silane may enter the capillaries of the substrate. There are many factors which may affect the viscosity of the PIBS latex/silane emulsion. The study of these factors in this research aimed to optimise the conditions to achieve a desired viscosity.

a. Effect of silane concentration on the viscosity of PIBS latex/silane emulsions

Figure 5.7 shows the relationship between apparent viscosity of the PIBS latex/IBTES emulsions and the shear rate at different silane concentrations. The concentrated emulsion exhibits shear thinning characteristics and the diluted emulsion exhibits Newtonian behaviour. According to Woodbridge,[126] the shear thinning behaviour is most preferred in emulsion paints and other coating products. High viscosity at low shear rate helps to increase the uniformity and the freedom from streaks. It also prevents the settlement of the particles in the emulsion. Low viscosity at high shear rate at the point of spraying will contribute to the easy spreading of the emulsion without air entrainment over the substrate surface.

At a concentration of 40% of silane, the PIBS latex/IBTES emulsion has very high viscosity. The viscosity of the emulsion containing 40% of silane is more than eight times higher than the viscosity of the emulsion made with 30% silane (the viscosity at low shear of 40% silane emulsion is 88.8 cps compared to 10.32 cps for the 30% silane emulsion). As the shear rate increases, the apparent viscosity of the emulsion containing 40% silane decreases dramatically.

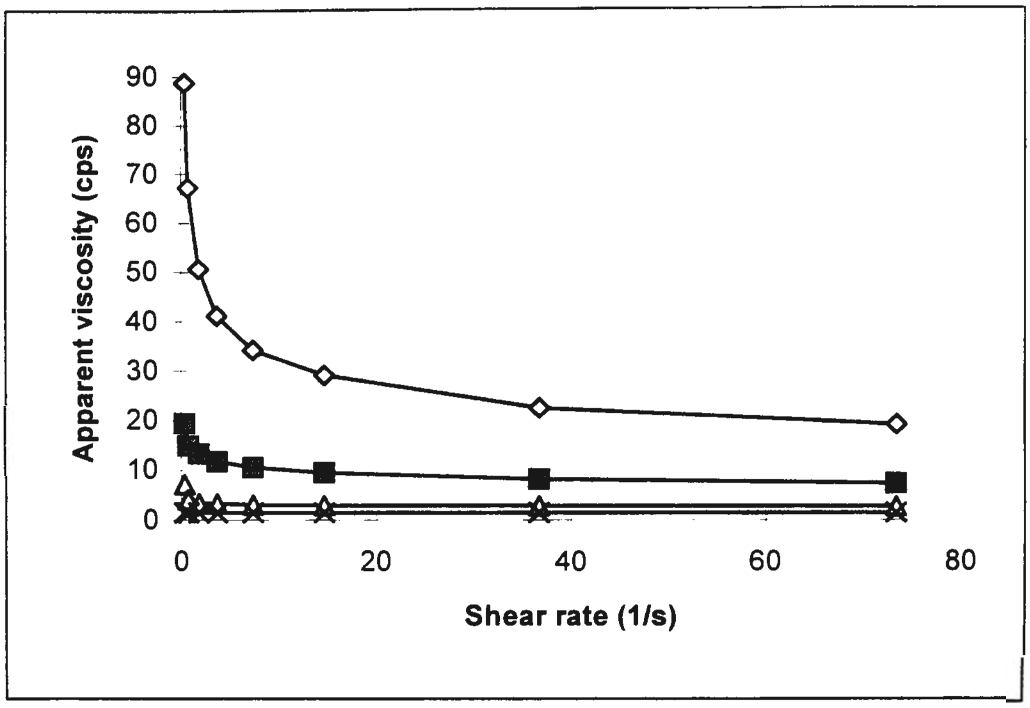


Figure 5.7. Apparent viscosity versus shear rate for PIBS latex/IBTES emulsions at different concentrations of silane

(◊) 40% silane
(▫) 30% silane
(Δ) 20% silane
(×) 10% silane

Figure 5.8 represents the flow behaviour for the PIBS latex/IBTES emulsion at different concentrations of silane by measurement of shear stress-shear rate. The flow behaviour of the emulsion changes when the emulsion which initially contained 40% silane was diluted. The viscosities of the emulsions containing 30 or 40% of silane are changed with shear. However, the viscosities of the diluted emulsions containing 10 or 20% silane are not changed with shear. The flow behaviour of the emulsion containing 40% silane changes from pseudoplastic to Newtonian when it is diluted to emulsions containing less than 20% silane.

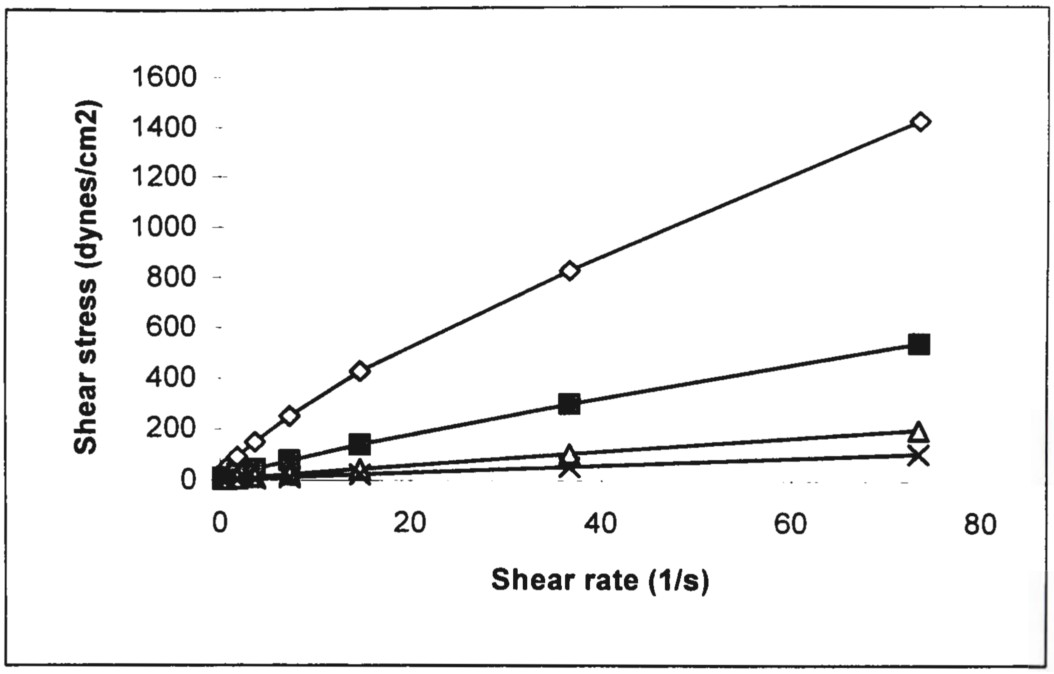


Figure 5.8. Flow behaviour of PIBS latex/IBTES emulsions at different concentrations of silane

(◊) 40% silane (Δ) 20% silane
( ) 30% silane (×) 10% silane

The results also show that the addition of silane into PIBS latex will result in a change of flow behaviour of the PIBS latex/silane emulsion. PIBS latex exhibits Bingham plastic behaviour with a yield stress at zero shear, even with a diluted latex containing 10% solid by weights (as discussed in 4.2.5). The flow behaviour of the PIBS latex indicates that under flow, the shear stress of the latex remains at the critical value, irrespective of the shear applied. When silane is added to the PIBS latex, the flow behaviour of the PIBS latex/silane emulsion changes. The PIBS latex/silane emulsion exhibits pseudoplastic behaviour (shear thinning) with no yield value. The emulsion has high viscosity at low shear and its viscosity decreases with the increase in the shear rate.

The flow behaviour of the PIBS latex/OTES emulsion is similar to that of the PIBS latex/IBTES emulsion as shown in Figure 5.9.

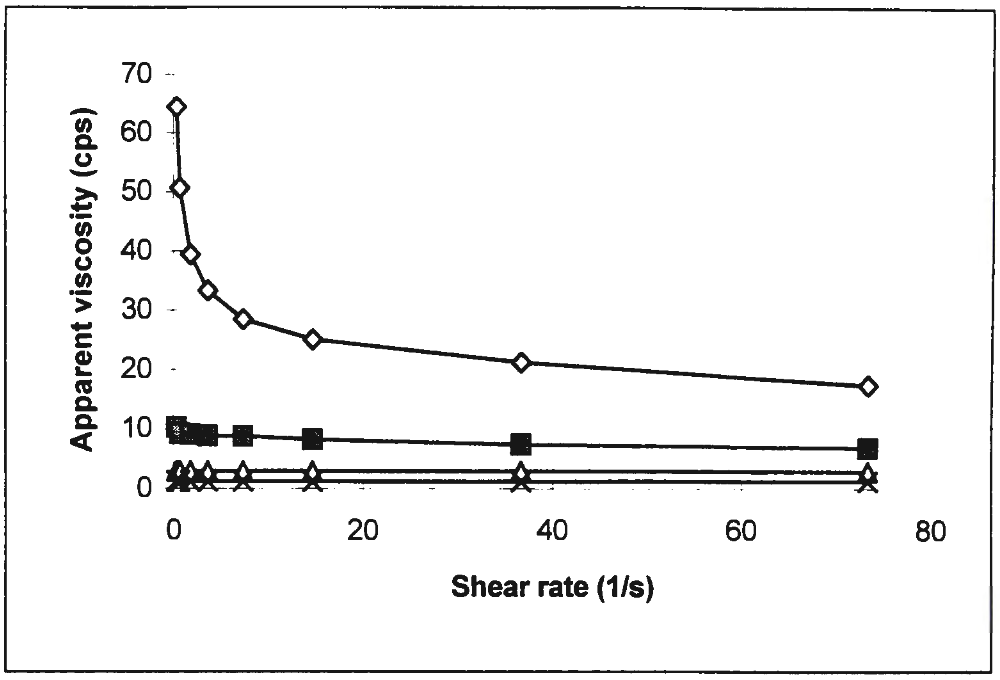


Figure 5.9. Apparent viscosity versus shear rate for PIBS latex/OTES emulsions at different concentrations of silane

(◊) 40% silane (Δ) 20% silane

( ) 30% silane (×) 10% silane

Concentrated PIBS latex/OTES emulsion containing 40% silane exhibits pseudoplastic behaviour. Diluted OTES emulsion containing 10% silane exhibits Newtonian behaviour as shown in Figure 5.10.

At the same concentration of silane, the viscosity of the PIBS latex/IBTES emulsion is higher than the viscosity of the PIBS latex/OTES emulsion as shown in Figure 5.11.

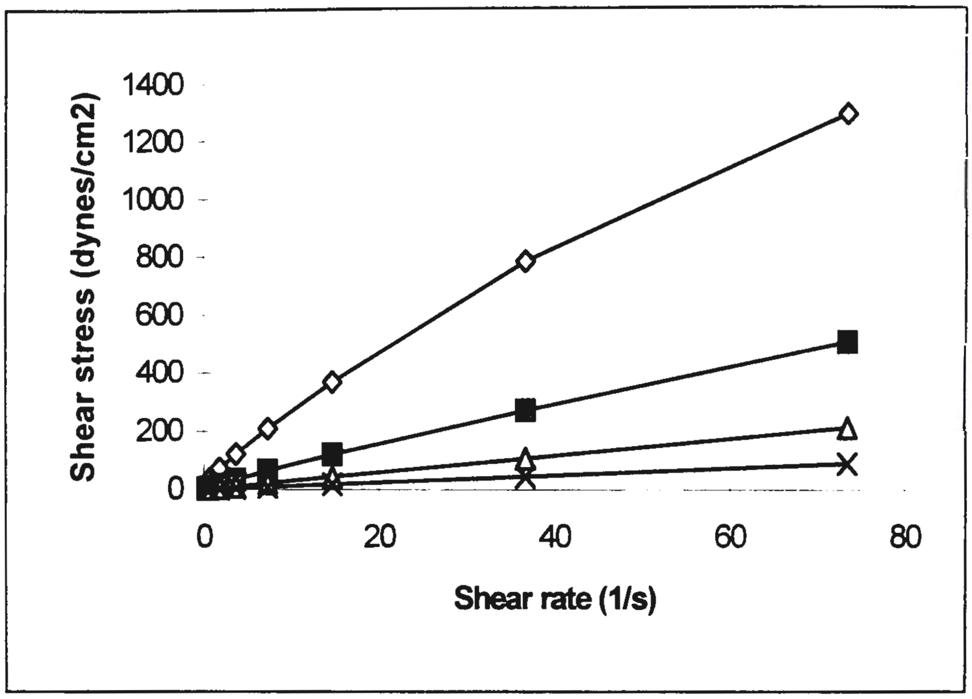


Figure 5.10. Flow behaviour of PIBS latex/OTES emulsions at different concentrations of silane

(◊) 40% silane (Δ) 20% silane

( ) 30% silane (×) 10% silane

The difference in viscosity between the two emulsions at low shear rate may be attributed to the effect of globule size and particle size distribution in the emulsion. According to Sherman,[127] apparent viscosity of the emulsion increases with a decrease in the globule size and is a function of size distribution. The PIBS latex/OTES emulsion has larger particles than the PIBS latex/IBTES emulsion. The particle size distribution of the OTES emulsion is broader than that of the PIBS latex/IBTES emulsion. The number of particles per unit volume of the OTES emulsion is lower than that of the IBTES emulsion. Therefore, the intermolecular interactions between particles which determines the viscosity of the emulsion become weaker in the OTES emulsion. This results in a lower viscosity of the PIBS latex/OTES emulsion compared to the viscosity of the PIBS latex/IBTES emulsion.

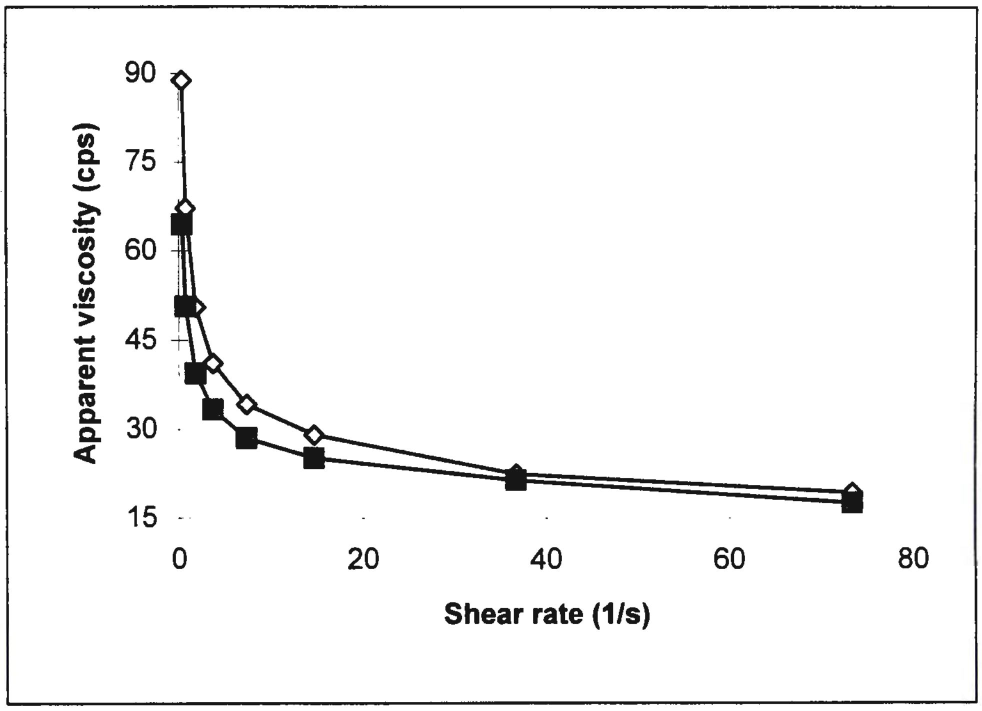


Figure 5.11. Apparent viscosity versus shear rate for PIBS latex/silane emulsion
(◊) PIBS latex/IBTES emulsion
( ) PIBS latex/OTES emulsion

b. Effect of preparation method on the viscosity of PIBS latex/silane emulsions

Figure 5.12 shows the effect of shearing time with the shear mixer on the viscosity of the PIBS latex/silane emulsion. The viscosity of the emulsion increases with the increase in shearing time and attains a maximum value at 20 minutes. Thereafter, the viscosity of the emulsion slowly decreases as the shearing time increases.

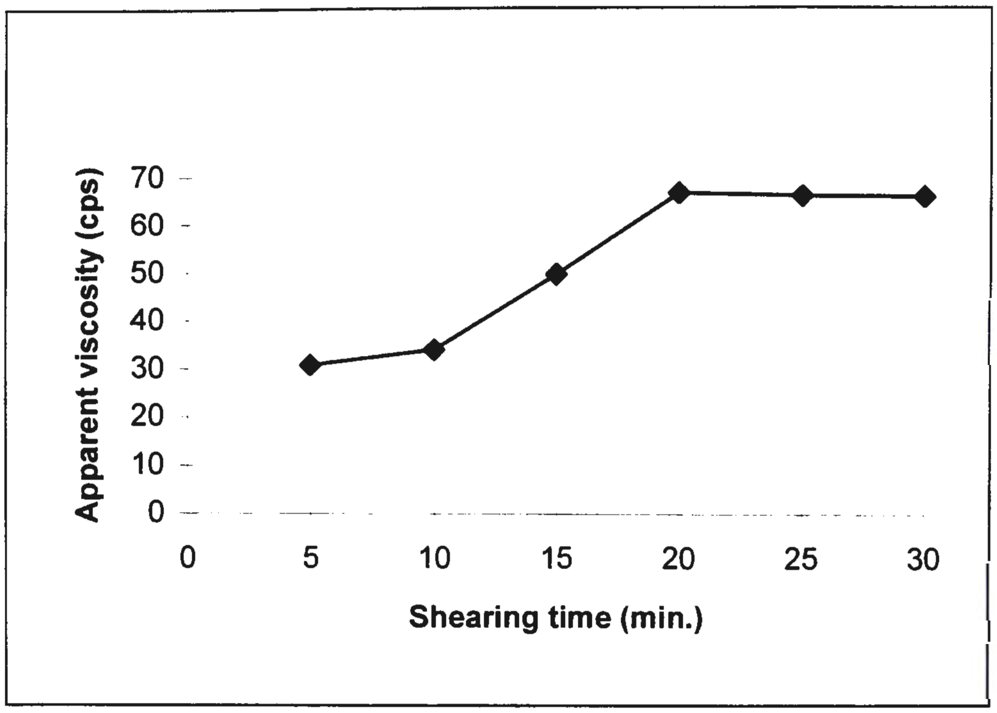


Figure 5.12. Effect of shearing time on the viscosity of PIBS latex/IBTES emulsion
(The viscosity was measured at the shear rate of 7.34 s^{-1}; the emulsion contained 18% solids and was prepared at 20,000 rpm)

At 20 minutes of shearing, the specific surface area or the number of particles per unit volume reaches a maximum value (ξ 5.1.1.4). At this stage, the van der Waals attraction between particles is strong enough to hold the particles close to each other. However, the attraction between particles is not sufficient to overcome the electrostatic repulsion between them. The particles are still moving freely as individual entities in the emulsion and the emulsion is stable. Coalescence does not occur at this time and the viscosity of the emulsion is high. As the shearing time increases after 20 minutes, collisions among the particles in the emulsion become more frequent, coalescence of the small particles occurs and large particles are formed. The presence of large particles in the emulsion at this stage reduces the number of particles in the emulsion. The interaction between particles in a unit volume becomes weaker and thus the viscosity of the emulsion decreases.

The method used to add silane into the latex has an effect on the viscosity of the emulsion. An emulsion which is prepared by injecting 2 grams of silane each time into the latex during the shearing process is more viscous than an emulsion which is prepared by adding silane drop by drop into the latex. The viscosity of the emulsion which is prepared by adding silane in very small increments into the latex is lower than the viscosity of the emulsion prepared by introducing silane in bulk to the latex before shearing as shown in Figure 5.13.

c. Effect of solids concentration on the viscosity of PIBS latex/silane emulsions

Figure 5.14 shows that the viscosity of the PIBS latex/silane emulsion depends on the concentration of solid in the emulsion. The viscosity of the emulsion increases with an increase in the solids concentration.

The solids concentration of the emulsion has an effect on the particle size and the PDMS of the PIBS latex/silane emulsions (as discussed in 5.1.1.1.a). Therefore, the viscosity of the PIBS latex/silane emulsion depends on the solids concentration of the emulsion.

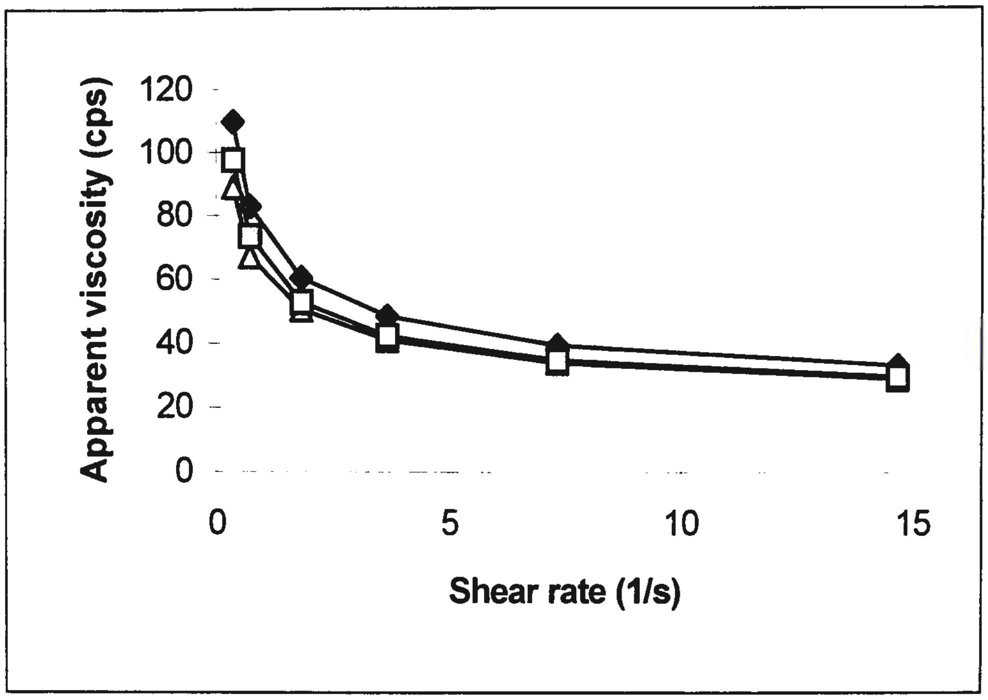


Figure 5.13. Effect of adding method on the viscosity of PIBS latex/IBTES emulsion

(The emulsion contained 18% solids and was prepared at 20,500 rpm)

(◊) Emulsion prepared by adding 2g of silane each time into PIBS latex

( ) Emulsion prepared by adding silane in bulk to PIBS latex

(Δ) Emulsion prepared by adding silane in small increments into PIBS latex

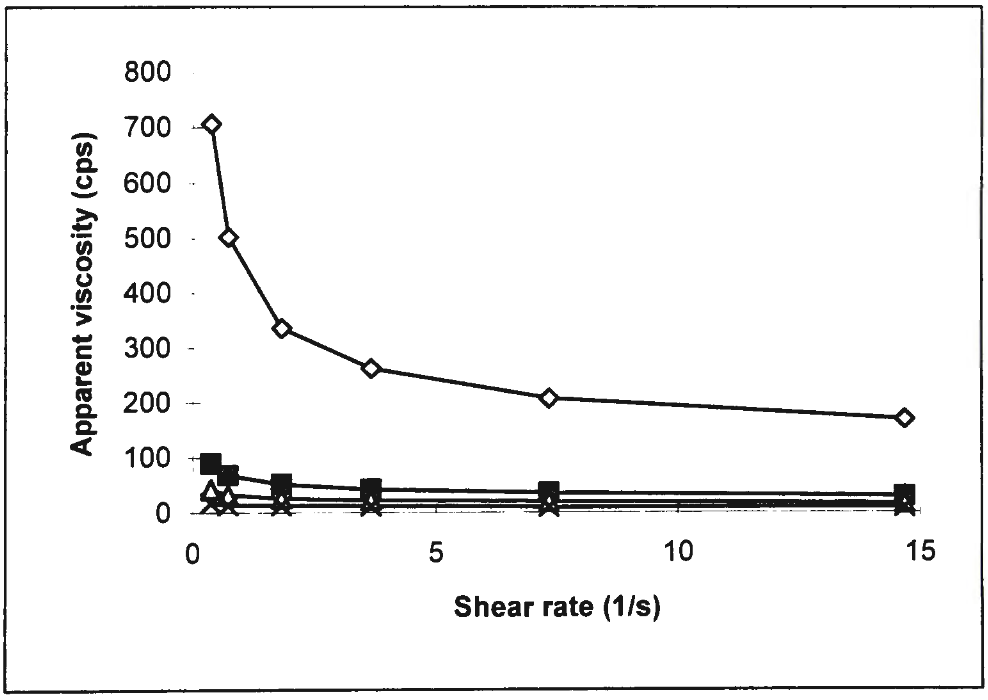


Figure 5.14. Flow behaviour of PIBS latex/IBTES emulsions at different concentrations of solids

(◊) 24% solids ( ) 12% solids

(Δ) 18% solids (×) 6% solids

At low solids concentrations of less than 12%, the PIBS latex/IBTES emulsion exhibits Newtonian behaviour. The viscosity of the PIBS latex/IBTES emulsion at solids concentrations of 12% or lower remains constant as the shear rate is varied. The results also show that the PIBS latex/IBTES emulsion exhibits a shear thinning (pseudoplastic) behaviour at solids concentrations of 18% or higher.

5.1.3.2. Viscosity of PDMS/silane emulsions

The relationship between apparent viscosity of PDMS latex/IBTES emulsion and shear rate is shown in Figure 5.15. The concentrated emulsion exhibits shear thinning characteristics and the diluted emulsion exhibits Newtonian behaviour. The flow behaviour of the PDMS/IBTES emulsion is similar to that of the PIBS latex/IBTES emulsion.

Unlike the PIBS latex/OTES emulsion, diluted PDMS latex/OTES emulsion begins to demonstrate a Newtonian behaviour at a silane concentration of 20% as shown in Figure 5.16. The difference in viscosity of the PDMS/silane emulsion and the PIBS latex/silane emulsion may be attributed to the difference in particle size of the emulsions.

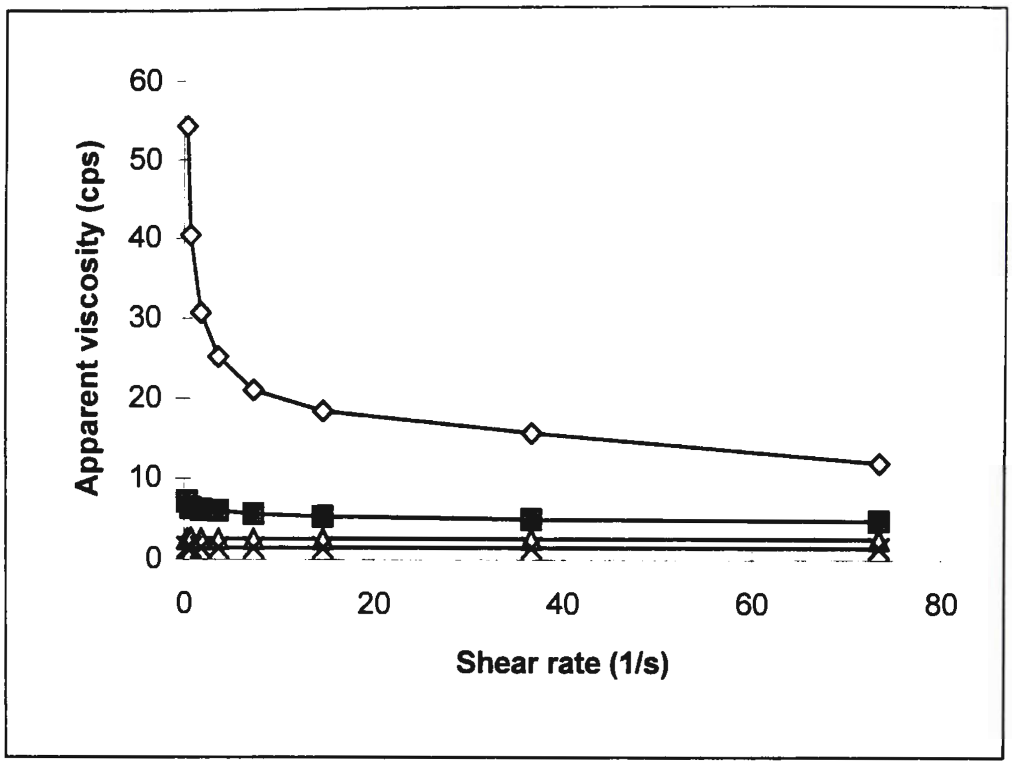


Figure 5.15. Apparent viscosity versus shear rate for PDMS /IBTES emulsions at different concentrations of silane

(◊) 40% silane (Δ) 20% silane
(□) 30% silane (×) 10% silane

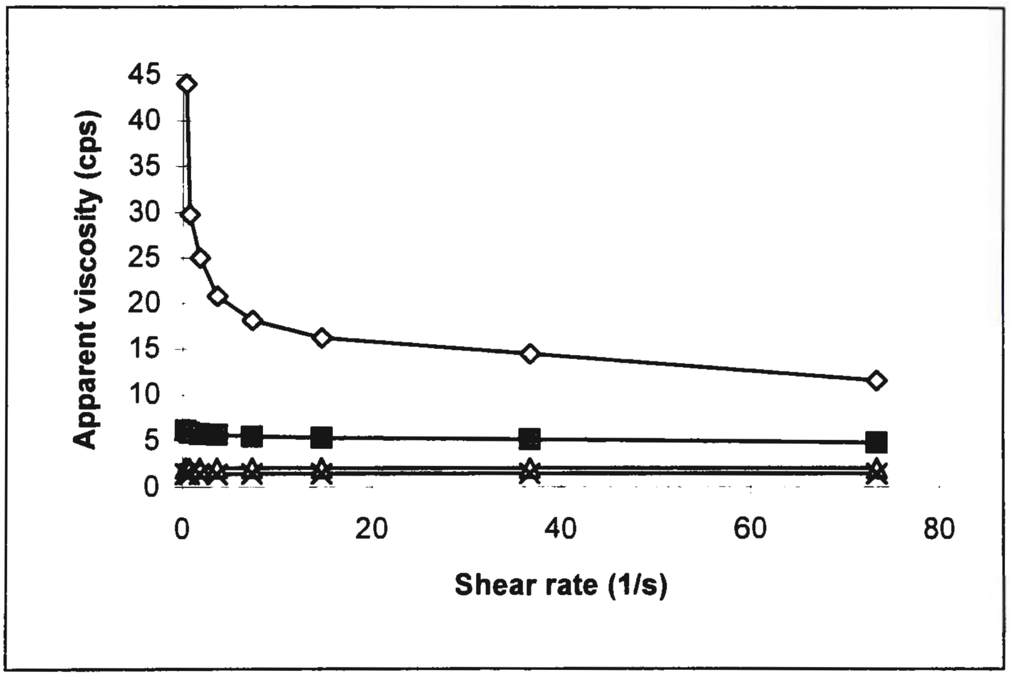


Figure 5.16. Apparent viscosity versus shear rate for PDMS /OTES emulsions at different concentrations of silane

(◊) 40% silane (Δ) 20% silane
( ) 30% silane (×) 10% silane

The particles in the PIBS latex/silane emulsions are smaller than the particles in the PDMS/silane emulsions. The number of particles in a unit volume of PIBS latex/silane emulsion is higher than that of PDMS/silane emulsion. The interaction between particles in PIBS latex/silane emulsions is stronger than the interaction between particles in PDMS/silane emulsions. Therefore, the viscosity of the PIBS latex/silane emulsion is higher than the viscosity of the PDMS/silane emulsion (Figure 5.17).

Figure 5.17 also shows that the silane structure has an effect on the viscosity of the PDMS/silane emulsions. The viscosity of PDMS/IBTES emulsion is higher than the viscosity of the PDMS/OTES emulsion. The size of the oil droplets in the PDMS/IBTES emulsion is smaller than the size of the oil droplets in the PDMS/OTES emulsion. Therefore, the viscosity of the PDMS/IBTES emulsion is higher than the viscosity of the PDMS/OTES emulsion.

The viscosity of the PDMS/silane emulsions depends on the PDMS concentration as the silane concentration is held constant at 40%. The viscosity of the PDMS/IBTES emulsion which contains 40% silane increases as the concentration of PDMS increases from 2% to 10%. The viscosity of the emulsion reaches a maximum value at a PDMS concentration of 10%. Thereafter, the viscosity of the emulsion decreases as the concentration of PDMS increases (Figure 5.18).

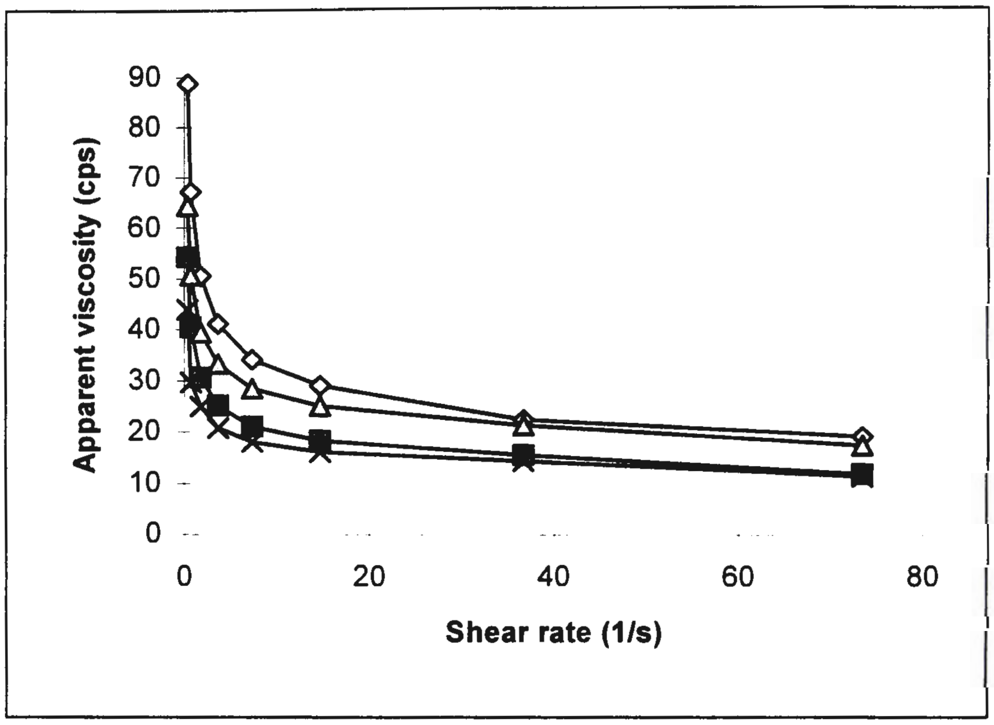


Figure 5.17. Apparent viscosity versus shear rate for novel emulsions

(◊) Concentrated PIBS latex/IBTES emulsion
(Δ) Concentrated PIBS latex/OTES emulsion
(□) Concentrated PDMS/IBTES emulsion
(×) Concentrated PDMS/OTES emulsion

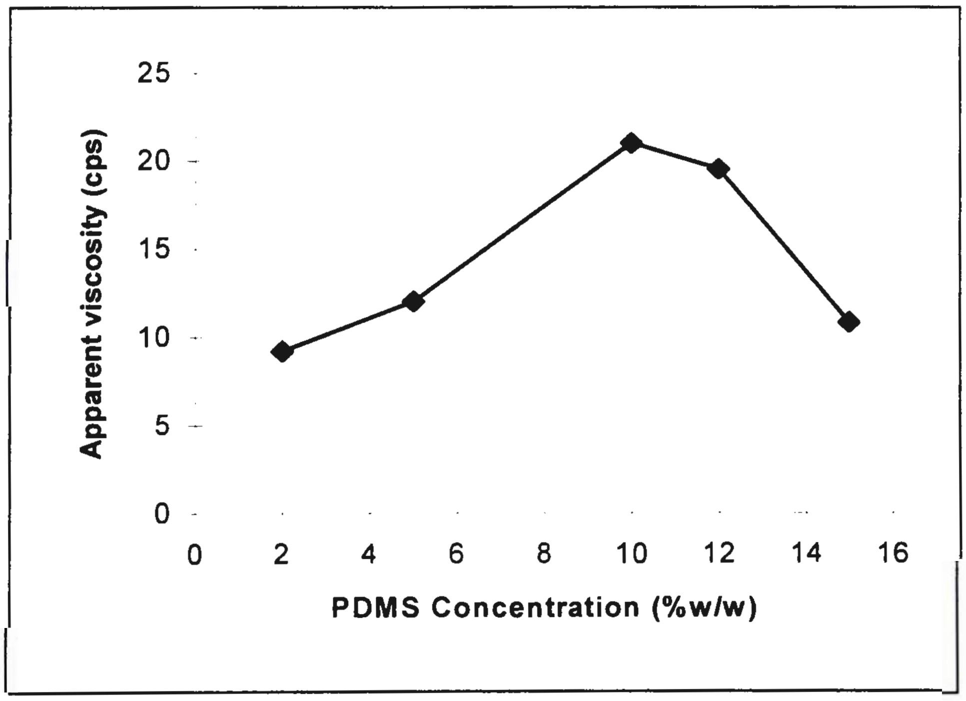


Figure 5.18. Effect of PDMS concentration on the viscosity of PDMS/IBTES emulsion

(The viscosity of the emulsion was measured at a shear rate of 7.34 s^{-1})

The concentration of the amine soap surfactant has an effect on the viscosity of the PDMS/silane emulsion (Table 5.6). The viscosity of the emulsion increases sharply as the surfactant concentration increases from 0.5 to 1.0%. Thereafter, the viscosity of the emulsion is not much changed with an increase in the surfactant concentration.

The speed of the shear mixer also has an effect on the viscosity of the PDMS/silane emulsion as shown in Figure 5.19. The result shows that the viscosity of the PDMS/silane emulsion increases with an increase in shearing speed of the shear mixer.

Surfactant concentration (%)	Apparent viscosity (cps)
0.5	14.3
1.0	19.5
1.5	21
2.0	22
2.5	22.5

Table 5.6. Effect of surfactant concentration on the viscosity of PDMS/IBTES emulsion
(The viscosity of the emulsion was measured at a shear rate of 7.34 s^{-1})

The effect of the shearing time of the emulsification process on the viscosity of the PDMS/silane emulsion is shown in Figure 5.20. The viscosity of the PDMS/IBTES emulsion reaches a maximum value after 10 minutes shearing. The viscosity of the emulsion then slowly decreases as the shearing time increases.

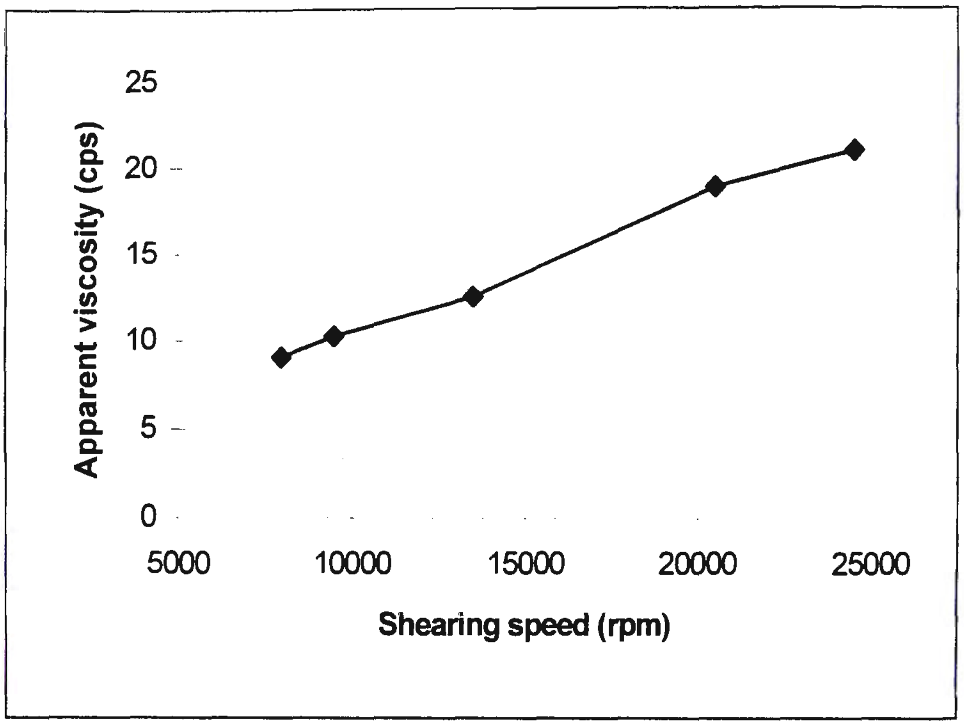


Figure 5.19. Effect of the speed of the shear mixer on the viscosity of PDMS/IBTES emulsion
(The viscosity of the emulsion was measured at a shear rate of 7.34 s^{-1})

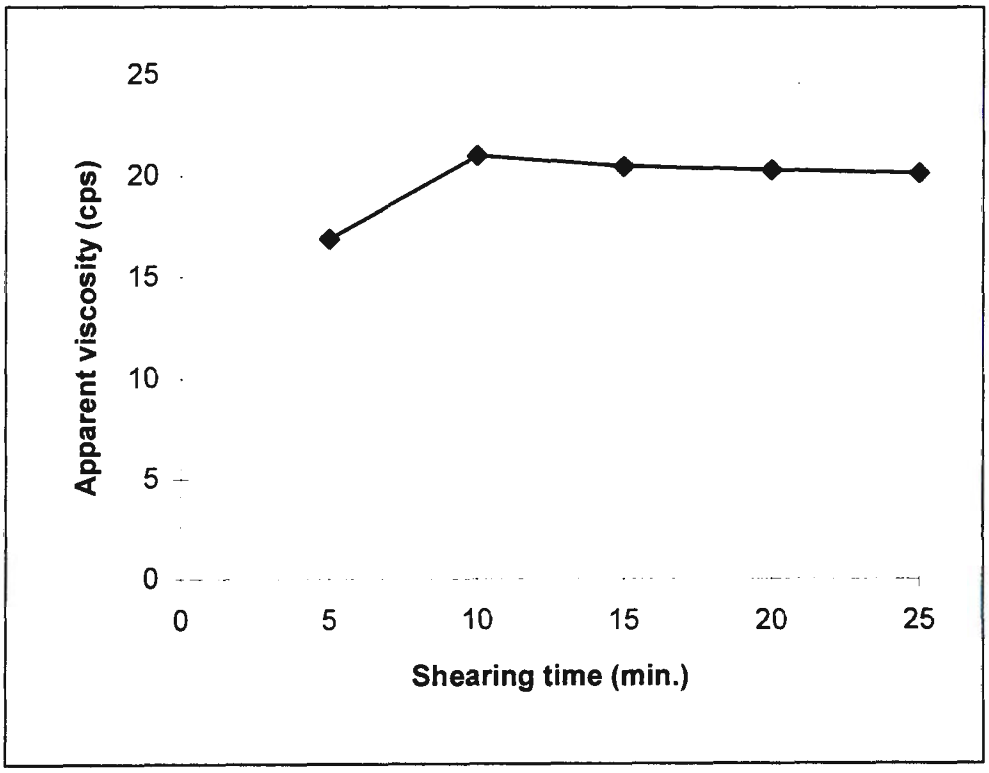


Figure 5.20. Effect of shearing time on the viscosity of the PDMS/IBTES emulsion
(The viscosity of the emulsion was measured at a shear rate of 7.34 s^{-1})

5.1.4. Preferred compositions for novel silane/siloxane emulsions

The above results from the particle size analysis and viscosity measurements show that for a desirable particle size and viscosity, the PIBS latex/silane emulsions should contain 18% PIBS solids and 40% alkylalkoxysilane. The most suitable speed of shear for the preparation of the emulsion is 20,500 rpm and the mixing of silane with PIBS latex should be carried out within 20 minutes.

The results also indicate that for a desired viscosity, the PDMS/silane emulsion should contain 10% silicone fluid, 40% silane, and more than 1% surfactant by weight. The suitable emulsification speed is 24,500 rpm and the emulsification process should be carried out in more than 10 minutes.

5.1.5. Freeze-thaw and tropical stability of novel silane/siloxane emulsions

5.1.5.1. Freeze-thaw stability of novel silane/siloxane emulsions

When emulsions are frozen, the freezing of the water phase causes the formation of long ice crystals. The oil globules are forced into narrow channels of unfrozen fluid between the ice crystals. The concentration of any electrolytes in the remaining unfrozen water increases, supercooling the residual water to an ever increasing extent and reducing the electric charge.[128] The growth of ice crystals forces the oil globules into contact with each other. The condition of the globule surface adjacent to the layer of adsorbed surfactants influences the subsequent behaviour of the emulsion.[129] The loss of mobility of the hydrophobic part of the adsorbed surfactant molecule occurs when the viscosity of the globule surface reaches that of a solid state. This prevents self-regeneration during the continuous deformation of the oil globules under pressure exerted by the ice crystals. Consequently, an uneven distribution of surfactants on the oil globule surface occurs. Coalescence begins at the part of the oil globule which is not covered by surfactants. Pospelova et al.[130] have shown that the extent of coalescence is influenced by the nature of the surfactant. Kistler[131] has also indicated that the coalescence of the oil globules on cooling depends on the extent of globule surface covered by surfactant and the nature of the oil phase. The degree of coalescence increases with the increase in the hydrophobic chain in the surfactant molecule which is attributed to the inhibition of self-generation as the viscosity in the vicinity of the globule surface is increased. The extent to which dehydration takes place is controlled by the length of the hydrophilic chain in the surfactant molecule which may render instability during freezing. The coalescence during freezing is minimised with an optimum balance between the hydrophilic and hydrophobic parts of the surfactant molecules.[127] Singleton et al.[132] have pointed out that both freezing and thawing rate have an influence on the stability. It has been found that rapid freezing and a moderate rate of thawing lead to greater instability than any other conditions. The nature and the melting point of the oil phase also affect the degree of coalescence.

The freeze-thaw stability tests on the novel emulsions showed that the PIBS latex/silane emulsions are sensitive to frost. The mechanism of coagulation during freezing may be attributed to the accumulation of dispersed phase particles which are rejected by the growing ice crystal lattice. The growing of the ice crystal lattice ultimately forces the primary PIBS particles into intimate contact with each other and so promotes coalescence. Barb and Mikucki[133] have worked on polystyrene emulsions and found that the particles which coagulated tended to be smaller. The more rapid the freezing and the more concentrated the emulsion, the larger are the particles formed. This research work was carried out with polystyrene latex emulsions and the principles may be extended to the PIBS latex/silane emulsions. In the PIBS latex/silane emulsions, the large number of small PIBS particles may contribute to the instability of the emulsions to freezing.

PDMS/silane emulsions were found to be more freeze-thaw stable than PIBS latex/silane emulsions. This may be due to the steric stabilisation effect[134] of PDMS at the water-oil interface. The high molecular weight PDMS molecule is flexible and thermally stable.[135] When PDMS/silane emulsions are frozen, PDMS creates a mobile phase and protects the charge on the emulsion droplets which causes sufficient repulsion to prevent coalescence. The particle sizes of the PDMS/silane emulsions are larger than the particle sizes of the PIBS latex emulsions and this may be another factor which contributes to the freeze-thaw stability of the PDMS/silane emulsions.

5.1.5.2. Tropical stability of novel silane/siloxane emulsions

Tropical stability of emulsions is a factor related to the fundamental metastability of emulsions. When the temperature increases, the viscosity of the emulsion changes and the gravitational effects become more pronounced. Therefore, in silane/siloxane emulsions, the polysiloxane particles which have a density greater than water may tend to sediment. Certain chemical changes may also occur in the emulsion and these changes may be accelerated by the heat at the experimental tropical temperature.

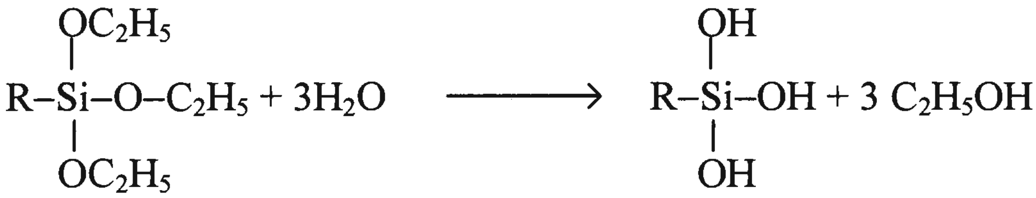
Tests carried out within this research showed that the novel silane/siloxane emulsions were stable at the experimental tropical temperature of 40°C. The emulsions were stored at 40°C for more than one month and there was no sign of separation or the formation of a serum on the surface of the emulsions after they were cooled down. The stability of the novel silane/siloxane emulsion at higher temperatures was also shown when the emulsion was heated to 90°C in an oil bath during headspace chromatography analysis. The emulsion still remained stable without any sign of the formation of a serum on the surface after being cooled down.

This tropical stability of the novel emulsions indicates that at a tropical temperature of 40°C, the gravitational effects or chemical changes have no effect on the stability of the emulsions. This conclusion is based on the assumption that no loss of water from the emulsion occurs.

5.1.6. The stability of alkylalkoxysilane in the novel silane/siloxane emulsion

Alkylalkoxysilanes are liable to undergo hydrolysis and a subsequent condensation reaction in the emulsion. This potential hydrolysis reaction makes it very difficult to keep alkylalkoxysilanes stable in aqueous solution.

The hydrolysis reaction of an alkylalkoxysilane is as follows:



$$\text{R}-\underset{\text{OC}_2\text{H}_5}{\overset{\text{OC}_2\text{H}_5}{\text{Si}}}-\text{O}-\text{C}_2\text{H}_5 + 3\text{H}_2\text{O} \longrightarrow \text{R}-\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}-\text{OH} + 3\ \text{C}_2\text{H}_5\text{OH}$$

Scheme 5.1 Hydrolysis reaction of alkyltriethoxysilane

One of the products from the hydrolysis of alkylalkoxysilanes in water is alcohol. Therefore, the degree of hydrolysis of the alkylalkoxysilane in the stored emulsion may be related quantitatively to the alcohol content of the emulsion. As part of this study, the degree of hydrolysis of the alkylalkoxysilane in the novel emulsions during storage was determined by the determination of ethanol content in an 11 month old PIBS latex/IBTES emulsion.

The headspace GC-MS chromatograms of IBTES and PIBS latex/IBTES emulsion are shown in Figure 5.21. In this figure, the peak at the retention time of 2.61 minutes may be attributed to ethanol, the peak at the retention time of 7.67 minutes may be attributed to isobutyltriethoxysilane and the peak at the retention time of 11.39 minutes may be attributed to octyltriethoxysilane.

IBTES emulsion was chosen for the study of the stability due to hydrolysis of the silane in the novel emulsion as the commercial IBTES contains almost no ethanol and its purity is higher than that of commercial OTES (Figure 5.21). The stability of IBTES is lower than the stability of OTES in an aqueous medium. Therefore, if IBTES is not liable to hydrolysis in the emulsion, OTES would be expected to be stable to hydrolysis in the emulsion under similar conditions of storage. The ethanol content in the PIBS latex/IBTES emulsion calculated from the standard curve was found to be 3.28% by weight, equivalent to 5.23% by weight of the IBTES which has been hydrolysed in the emulsion during storage. The result shows that more than 94% of the IBTES in the emulsion was not hydrolysed after the emulsion had been stored for 11 months at room temperature. This result also confirms the previous study by Wilson[136] which indicated that emulsions containing alkylalkoxysilanes are "hydrolytically" stable if the pH of the emulsion is maintained in a predetermined stable range of 6-8. It also indicates that the addition of a buffering agent is not necessary to maintain high effective levels of active silane content in the novel PIBS latex/silane emulsions.

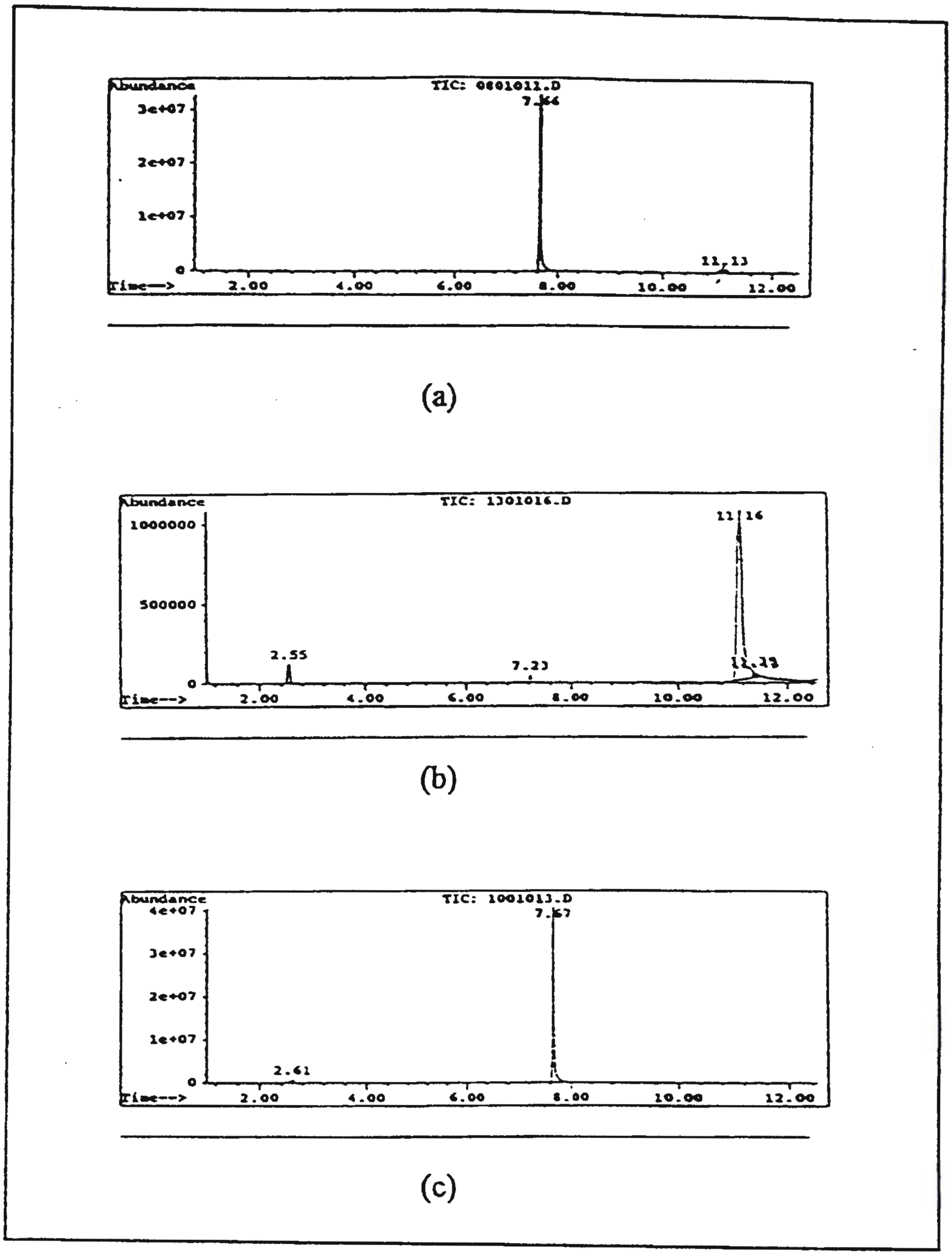


Figure 5.21. Headspace GC-MS chromatogram of (a) IBTES, (b) OTES and (c) PIBS latex/ IBTES emulsion which was stored at room temperature for 11 months

5.2. The stability of novel silane/siloxane emulsions

5.2.1. The stability of PIBS latex/silane emulsions

PIBS latex/silane emulsions are electrostatically stabilised systems. The electrostatic repulsions between the PIBS particles and the silane droplets overcome the interparticle attractions between them. The strong repulsion keeps the emulsion particles apart at a distance where the attraction between them remains just strong enough to hold them close but is not enough to cause coalescence. The particles still move freely and individually in the emulsion.

In PIBS latex/silane emulsions, the PIBS latex particles are stabilised by strong electrostatic force repulsion between the particles (ξ 4.3). The electrostatic repulsion between silane monomer droplets arises from the presence of the charged PIBS particles and the ionised sulphonate end groups of SDBS which accumulate at the oil-water interfaces. The presence of the PIBS particles in the emulsion plays an important role in the stability of the PIBS latex/silane emulsion. The PIBS particles may prevent the thinning of the liquid film between the silane droplets. They contribute to the reduction of the interfacial tension of the system (ξ 4.2.2) and lead to high zeta potential (Table 5.1) and a stabilising effect.

5.2.2. The stability of PDMS/silane emulsions

PDMS plays an important role in the stabilisation of this emulsion. In PDMS/silane emulsions, PDMS and silane form droplets with the aid of amine soap and adsorb at the surface of the oil droplet. The PDMS droplets and silane droplets are stabilised by the balance between the van der Waals attractions and the electrostatic repulsions between oil droplets in combination with the steric stabilisation effect of the free PDMS molecules in the emulsion. The electrostatic charge at the surface of the oil droplets results from the presence of amine soap molecules at the water-oil interface. The layer of ionised carboxyl groups and the diffuse ion atmosphere of compensating counter ions surrounds each oil droplet and forms the electrical double layer. The electrostatic repulsion between oil droplets occurs when their electrical double layers overlap. In the PDMS/silane emulsion, the electrostatic repulsions between oil droplets are strong as shown by the relatively high absolute value of the zeta potential of the emulsion (ξ 5.1.2). The steric stabilisation effect in the PDMS/silane emulsion is caused by the adsorption of PDMS polymer at the surface of the oil droplet. According to Bass,[137] PDMS has a helical structure in which the siloxane backbone is flexible and partially ionic. PDMS also exhibits very low intermolecular attraction. Therefore, the layer of polymeric PDMS adsorbed around the oil droplet generates a repulsive force when two oil droplets approach each other through a Brownian encounter. This steric stabilisation effect of the PDMS contributes to the high freeze-thaw stability of the PDMS/silane emulsions (ξ 5.1.4.1). The schematic representation of the steric stabilisation of an oil droplet by PDMS is shown in Figure 5.22.

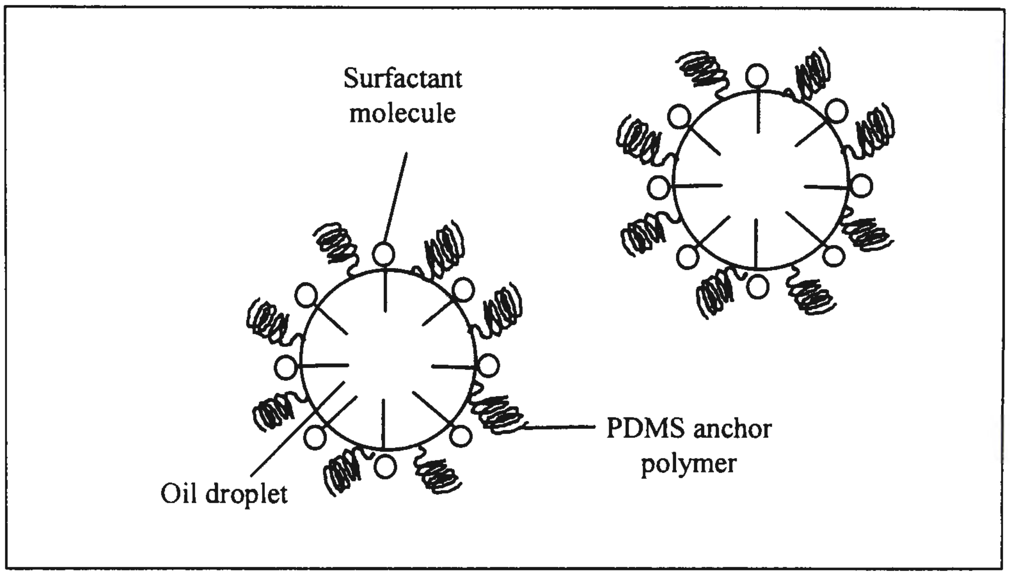


Figure 5.22. Schematic representation of the steric stabilisation of an oil droplet by PDMS

PDMS/silane emulsions are stable for more than one year. This may be attributed to the combination of the electrostatic repulsion between oil droplets and the steric repulsion of the adsorbed PDMS layer on the oil droplets overcomes the attraction between emulsion droplets in the PDMS/silane emulsion.

The particle size analysis shows that the PDMS/silane emulsions have more large particles than the PIBS latex/silane emulsions. The PDMS/silane emulsions have lower viscosity and lower zeta potentials than the PIBS latex/silane emulsions. All of these factors indicate that PDMS/silane emulsions may be less stable than PIBS/silane emulsions during long term storage.

CHAPTER SIX

The effectiveness of novel silane/siloxane emulsions for concrete protection

6.1. Evaluation of the performance of novel emulsions

An evaluation of the performance of the impregnants was conducted in this study. The performance was examined in terms of the beading effect, the penetration depth of the impregnants, and the water absorption of the concrete substrates treated with novel emulsions and hydrocarbon solutions containing the same concentration of silane. Alkali stability of the impregnants, chloride ion resistance due to the impregnant and the effect of UV radiation on impregnants were also tested. The effectiveness of the novel emulsions for concrete protection was evaluated by a comparison of the results obtained from the substrates treated with novel emulsions with those obtained from the substrates treated with silane solutions in organic solvent.

6.2. The application mechanism of silane/siloxane emulsions

When a silane/siloxane emulsion is applied to a concrete substrate, several reactions simultaneously occur:

(a) the emulsion breaks,[138] and siloxane, silane and water are absorbed into the concrete substrate by capillary suction;

(b) a polysiloxane film is formed on the concrete surface;[139]

(c) the silane partially evaporates;

(d) silane molecules react with each other and with the concrete substrate.

As soon as the emulsion spreads over the concrete surface, emulsion ingredients are absorbed into the concrete. The absorption of the silane and water into the concrete substrate by capillary forces is the fastest reaction compared to the absorption of the polysiloxane due to their small molecular weight and high spreadability. The second fastest reaction is the formation of the polysiloxane film (from PIBS particles or PDMS droplets) on the concrete surface. The hydrolysis of the monomeric alkylalkoxysilane, followed by the subsequent condensation reaction of silanol intermediates in the capillaries and pores inside the concrete substrate is very slow and may take days to be completed. The evaporation of the silane during application is the slowest reaction. The evaporation of the silane may occur faster than the condensation reaction only under unfavourable application conditions such as low humidity, high winds and/or high temperature. High temperature, whilst promoting evaporation, also speeds up the condensation of silanols into oligomeric siloxanes and accelerates film forming of the polysiloxane on the concrete surface. This will significantly reduce the evaporation of the silane inside the capillaries and pores to the treated surface. It has been shown by the work of McGettigan,[140] that the loss of high boiling silane due to evaporation, even under unfavourable application conditions is so minimal that it can be ignored in field application. The absorption of the polysiloxane into the concrete substrate is much slower than the absorption of silane due to its high molecular weight. Therefore, most of the polysiloxane remains on the treated surface and this will have a beneficial effect on the beading effect of the treated concrete.

The loss of water either by absorption into the concrete substrate or evaporation into the atmosphere causes the suspended polysiloxane particles (or droplets) to become crowded together to form a hydrophobic film on the treated surface. Film formation is a complex process and the mechanism of film formation has not been completely elucidated. The earliest theory of film formation was developed by Dillon et al.[141] According to this theory, the main energy required for particle coalescence is produced by surface tension forces as the total surface area decreases. The theory uses Frenkel's equation:[142]

$$\theta^2 = 3\gamma t/2\pi\eta r \qquad (6.1)$$

where θ is the half-angle of coalescence (Figure 6.1), γ is the surface tension, r is the particle radius and η is the particle viscosity. θ^2 was determined as a function of particle radius r. Equation 6.1 shows that the pressure related to θ on the particles varies inversely with the polymer particle radius.

An alternative theory according to Brown[143] postulated that polymer particles would coalesce if the driving force provided by capillary pressure is sufficient to overcome the resistance of the particles to deformation. The nature of the forces involved in the coalescence of the particles is shown in Figure 6.2. According to this theory, the maximum modulus for film formation depends inversely on the particle radius r.

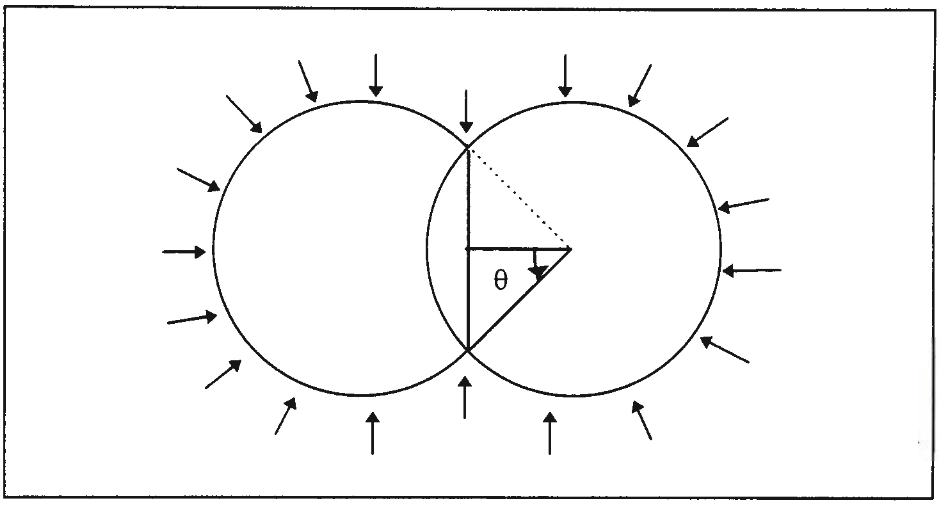


Figure 6.1. Coalescence of spherical particles by viscous flow caused by surface tension forces

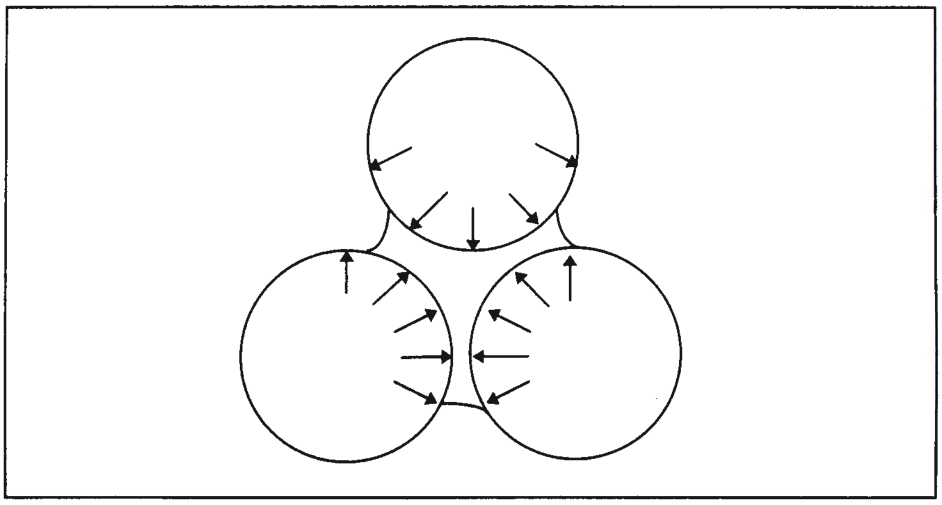


Figure 6.2. Coalescence of spherical particles caused by capillary forces

Voyutskii[144] indicated that there is an additional force that is considered as assisting film formation. This force is called 'autohesion', which is the mutual inter-diffusion of free polymer chain-ends across the particle-particle interface in the coalesced film. Vanderhoff[145] pointed out that both polymer-water and water-air interface play a part in film formation and the first force to be overcome during evaporation is the repulsion force between particles which arises from the electrical double layer overlap.

Sheetz[146] showed that during the film formation process, water evaporates until the system becomes so concentrated that the repulsion between particles is overcome and flocculation begins. At this point the spheres in the surface begin to emerge from the liquid and are consequently subjected to capillary forces. The capillary force G consists of G_n which is perpendicular to the surface and G_p which is parallel to the surface. G_n tends to push the particle in a direction normal to the surface, exerting a compression on the matrix of particles below the surface which contract or deform and force water to the surface. Simultaneously, G_p tends to distort the surface layers of particles so that the gaps between them are closed (Figure 6.3). If the free energy of the polymer-water interface is significant, wet sintering will contribute to the forces fusing the particles in the early stage of the compaction process. During this time, water is also diffusing through the particles on the surface and evaporating. This exerts a compacting force normal to the surface. Ultimately, water can only leave by diffusion through the particles as the compaction grows and the compressive pressure compacts the polymer film with no void spaces. After compression, the interfaces remain intact and it takes several days before the final equilibrium is reached as either the adsorbed surfactants congregate together if there is a large surplus of surfactant or become dispersed evenly throughout the film where only a small quantity of surfactant has been used.

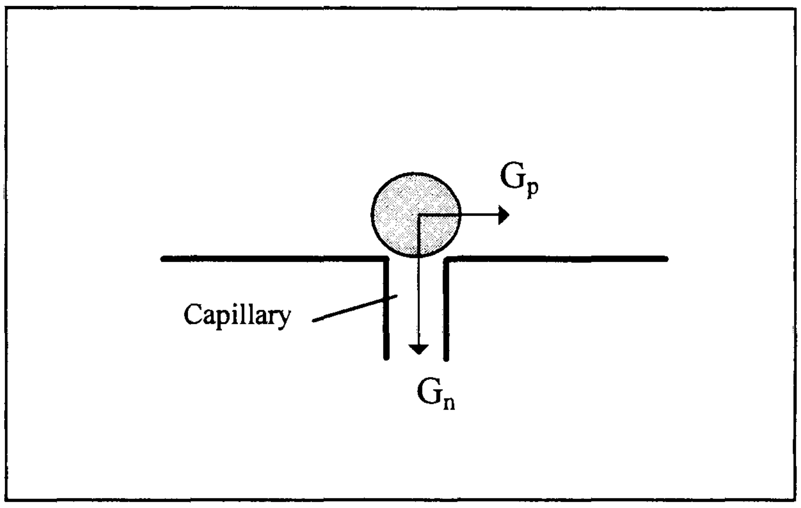


Figure 6.3. Schematic representation of the capillary force

The rate of film formation depends on the water absorption rate of the substrate, the quantity of emulsion, the temperature, the type of surfactant, and the particle size of the emulsion. If the water absorption rate is slow, it may allow polysiloxane particles or droplets to have sufficient time to assume optimum packing and, therefore, maximum binding and film integration. If the water absorption rate is fast, or if the size of the capillaries or pores of the concrete substrate are greater than the emulsion droplets, it is probable that the emulsion will quickly impregnate the substrate, leaving a weak or poorly integrated film on the surface. Increases in temperature will accelerate the evaporation rate of water and silane whilst only slightly affecting the diffusion rate of water and silane through the polysiloxane film. During the film forming process, surfactants will not only remain at the film surface, but also migrate into the concrete substrate where they could interfere with wet adhesion of the film. The particle size of the emulsion plays a major role in film formation and integration according to the theories developed by Dillon et al.[141] and Brown.[143] Both these theories imply that the pressure on the particles to coalesce increases with small particles. Emulsions with small polymer particles will produce films where the particles are more closely packed. Water and silane must diffuse through a continuous surface film to evaporate. The rate of diffusion through the surface film is slower than the rate of evaporation at the air-emulsion interface. Therefore the film formation will effectively reduce the evaporation of alkylalkoxysilane under the PIBS film.

6.3. Factors affecting the performance of silane/siloxane emulsions

The effectiveness of silane/siloxane emulsions for the protection of reinforced concrete depends on a number of factors such as the choice of the silane, the stability of the silane in the emulsion and the effect of surfactant on the beading effect exhibited by the treated concrete.

The choice of the silane plays an important role in the performance of silane/siloxane emulsions as it has a great influence on the water repellency and the alkali stability of the impregnant in the treated concrete. Isobutyltriethoxysilane (IBTES) and octyltriethoxysilane (OTES) have been chosen as the active ingredients in the novel silane/siloxane emulsions. The reasons for choosing IBTES and OTES are due to (a) their low volatility and therefore the loss of the silane during application is minimised, (b) the rate of hydrolysis of IBTES and OTES in an aqueous medium is very slow compared to alkyltrimethoxysilanes,[147] (c) their high degree of water repellency (ξ 6.4) and good resistance to hydroxide attack (ξ 6.5) due to the isobutyl and octyl group, (d) their small molecular size in a comparison to the capillaries and pores in concrete[148] and (e) their commercial availability.

In silane/siloxane emulsions, the alkylalkoxysilane is hydrolysable. In an acidic or basic aqueous medium, the hydrolysis of the alkoxy group occurs and alcohol is produced. Therefore, if the pH of the emulsion is not neutral, the active silane may hydrolyse to silanol and polymerise. As a result, the silane content in the emulsion would be reduced during storage. The pH of the novel silane/siloxane emulsions were maintained at pH~7 without the use of a buffer. Test results (ξ 5.1.5) showed that the silane remained substantially unhydrolysed and its concentration in the emulsions was not changed during storage for many months. In the PIBS latex, the surfactant SDBS is a wetting agent. The PIBS latex was cleaned in a purification process before use in making PIBS latex/silane emulsions and thus the concentration of "free" SDBS in the final emulsions was very low. The remaining SDBS in the PIBS latex/silane emulsion has little effect on the treated concrete (as shown in 6.3 and 6.4). The hydrophobic layer under the very surface of the concrete treated with the novel emulsions was not wetted when the "impregnated part" of the cross-section of the treated specimen was immersed in water. This indicates that the SDBS surfactant and amine soap when used at low concentration, caused no "wetting effect" at the very surface of the treated concrete.

The combination of alkylalkoxysilane and polysiloxane used to make novel emulsions has some advantages. Firstly, a high penetration depth was achieved due to the low molecular weight of the silane. Secondly, a satisfactory early water repellency was achieved due to the fast film-forming of the polysiloxane on the treated surface. Thirdly, the use of the polysiloxane makes the emulsification of the silane easier and a determination of the optimum HLB value at which the silane may be emulsified becomes unnecessary.

6.4. The beading effect and the penetration depth of the water repellent

The beading effect and the penetration depth of the impregnant for the treated concrete blocks is shown in Table 6.1. The penetration depths of the emulsions are lower than that of the solutions. This can be explained by the presence of the polysiloxane in the emulsions. Some PIBS particles in the emulsions would have an average diameter of over 10 nm and are larger than the concrete gel pores which have an average diameter of 1.5-2.0 nm.[148] Therefore, when the emulsion is applied onto the concrete substrate, the emulsion breaks and some of polysiloxane remains on the surface of the concrete substrate.

The lower penetration depth of the emulsions may also be attributed to the lower spreadability of the emulsion compared to the silane solution. According to Washburn,[149] the rate at which a liquid will rise in a vertical cylindrical capillary of a solid substrate, assuming the absence of wall slippage effects is shown by:

$$dh/dt = r(\gamma\cos\theta - gh\rho)/4\eta h \qquad (6.2)$$

where dh/dt is the rate of penetration into capillaries, h is the height of rise in time t, γ is the surface tension of the liquid, r is the radius of the capillary, θ is the contact angle, g is the gravitational constant, $\rho = \rho_1 - \rho_2$ is the difference in density between the rising liquid (ρ_1) and the surrounding fluid (ρ_2) and η is the viscosity of the liquid. Equation (6.2) shows that the rate of penetration of a liquid into a capillary depends on the viscosity of the liquid. The viscosity of the emulsion is higher than that of the hydrocarbon solvent in silane solution. Therefore, the emulsion exhibits less spreadability than the silane solution. As a result, the penetration depth of the emulsions is lower than that of the silane solutions.

Impregnants	Concentration of silane (% by weight)	Penetration depth (mm)	Beading effect
IBTES solution	40%	6.5	3
	20%	3.5	3
PIBS latex/IBTES emulsion	40%	6.0	3
	20%	3.0	3
PDMS/IBTES emulsion	40%	5.5	2
	20%	2.8	2
OTES solution	40%	6.0	2
	20%	3.0	2
PIBS latex/OTES emulsion	40%	5.5	2
	20%	2.8	2
PDMS/OTES emulsion	40%	5.0	1
	20%	2.5	1

Table 6.1. The beading effect and penetration depth for the treated concrete blocks

The penetration depth also depends on the nature of the alkyl group of the active alkylalkoxysilane. The larger the alkyl group, the lower the penetration depth obtained. This is shown by the penetration depth in concrete treated with silane solutions and emulsions. Therefore, octyltriethoxysilane emulsions with an eight carbon alkyl group exhibit a lower penetration depth than those of isobutyltriethoxysilane emulsions with a four carbon alkyl group. The penetration depth increases with an increase in silane concentration. The beading effect of the PIBS latex/IBTES emulsions is similar to the solutions containing the same concentration of the silane in hydrocarbon solvent (Table 6.1).

The molecular weight of the siloxane has an effect on the penetration depth of the silane/siloxane emulsions. The penetration depth of PDMS/silane emulsions with PDMS having a molecular weight of 13,650 is lower than the penetration depth of the PIBS latex/silane emulsions in which the molecular weight of the PIBS particles lie in the range between 800 and 4,000. The beading effect of the treated concrete with PDMS/silane emulsions is better than the concrete treated with silane solutions or PIBS latex/silane emulsions. This indicates that the presence of the silicone fluid and amine soap at the surface of the concrete increases the beading effect of the treated substrates. The PDMS/silane emulsions provide a better beading effect than PIBS latex/silane emulsions due to the effect of the surfactant remaining on the surface. In the PIBS latex/silane emulsions, SDBS is a wetting agent, whilst the amine soap of oleic acid in the PDMS/silane emulsions is a deactivatable surfactant. Following treatment of the concrete, the amine soap decomposes as the morpholine or ammonia evaporates and leaves the hydrophobic oleic acid on the concrete surface. However, any SDBS in the PIBS latex/silane emulsion remains on the treated surface and decreases the beading effect.

The penetration depth in mortar discs is higher than the depth in concrete substrates (Table 6.2). This indicates that the penetration depth depends largely on the compaction of the substrate and the resultant capillary and pore size.

Impregnants	Concentration of silane (% by weight)	Penetration depth (mm)	Beading effect
IBTES solution in hydrocarbon	40% 20%	12.0 8.5	3 3
PIBS latex/IBTES emulsion	40% 20%	11.0 7.5	3 3
PDMS/IBTES emulsion	40% 20%	9.0 6.5	2 2
OTES solution in hydrocarbon	40% 20%	9.0 7.0	2 2
PIBS latex/OTES emulsion	40% 20%	7.0 6.5	2 2

Table 6.2. The beading effect and penetration depth for the treated mortar discs

6.5. Water absorption of the treated concrete

Figure 6.4 represents the relationship between the time of water absorption test and the percentage weight gain of the treated and untreated concrete over 35 days for isobutyltriethoxysilane solution and emulsion. The water absorption of the untreated concrete increases sharply during one day, then slows down and becomes nearly constant after 7 days. The water absorption performance of concrete substrates treated with IBTES solution and PIBS latex/IBTES emulsion exhibit very similar characteristics to each other. Figure 6.5 shows that the water absorption performance characteristics of the IBTES emulsions are superior to the IBTES solution of the same concentration of isobutyltriethoxysilane. This may be attributed to the formation of polysiloxane film on the surface of the concrete treated with emulsion and the filling of the larger pores in the surface layer of the treated concrete by PIBS particles or PDMS.

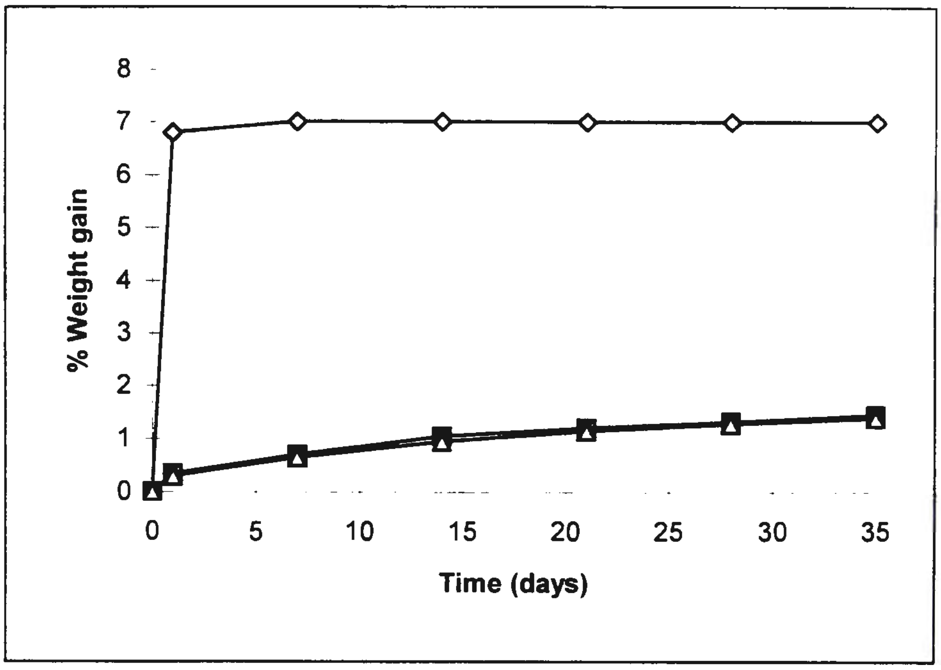


Figure 6.4. Water absorption of treated and untreated concrete

(◊) untreated concrete
(□) 40% IBTES solution
(Δ) 40% PIBS latex/IBTES emulsion

As shown in Figure 6.6, the water absorption of concrete samples treated with octyltriethoxysilane emulsion is lower than those treated with the isobutyltriethoxysilane emulsion. This may be attributed to the fact that the large octyl group is more hydrophobic than the smaller isobutyl group.[140] This also explains why concrete substrates treated with octyltriethoxysilane impregnants exhibit a better beading effect than those treated with isobutyltriethoxysilane impregnants (Table 6.1).

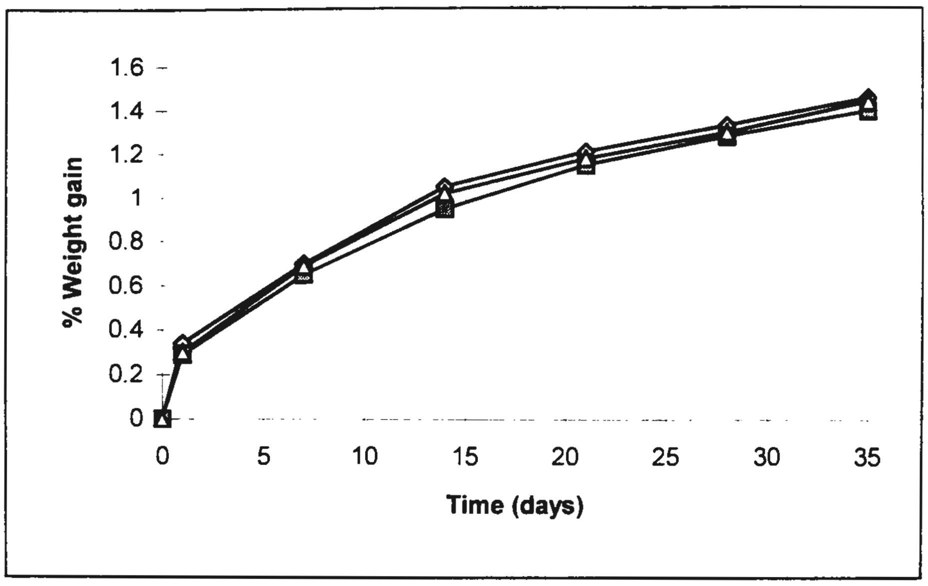


Figure 6.5. Water absorption of concrete treated with IBTES impregnants

(◊) 20% IBTES solution
(Δ) 20% PDMS/IBTES emulsion
(□) 20% PIBS latex/IBTES emulsion

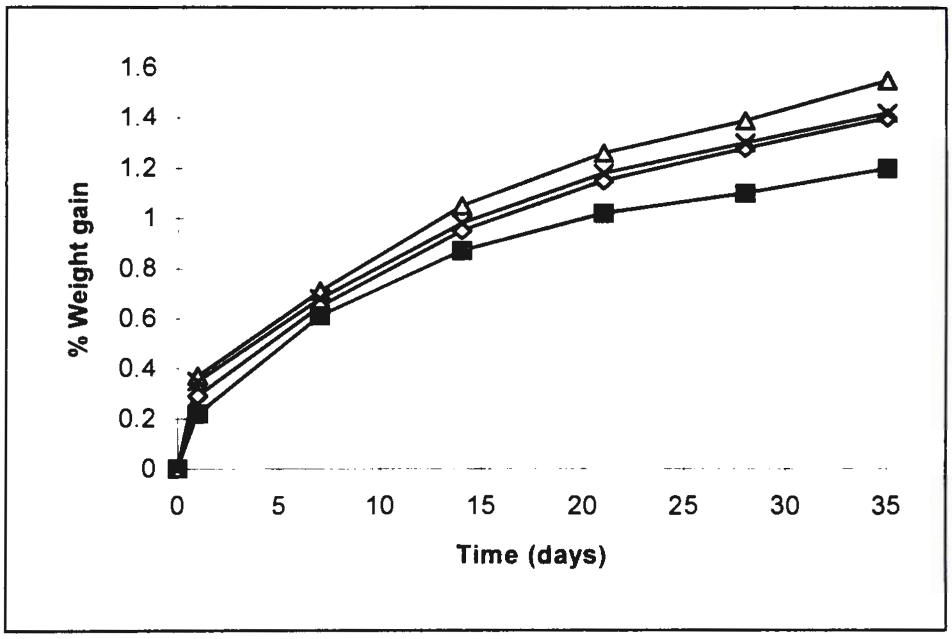


Figure 6.6. Water absorption of concrete treated with PIBS latex/silane emulsions

(□) 40% PIBS latex/OTES emulsion
(◊) 40% PIBS latex/IBTES emulsion
(×) 20% PIBS latex/OTES emulsion
(Δ) 20% PIBS latex/IBTES emulsion.

The presence of the surfactant in PIBS latex/silane emulsions appears to have no effect on the water absorption of the concrete treated with diluted emulsion. This is evidenced by the water absorption of the concrete treated with the diluted PDMS/OTES emulsion being higher than that of the concrete treated with PIBS latex/OTES emulsion (Figure 6.7). This is interesting in that the PIBS latex/silane emulsion would contain some residual SDBS. On the concrete surface this would exhibit some wetting effect in a comparison to the deactivatable amine soap in the PDMS/silane emulsion. The higher water absorption of the concrete treated with PDMS/OTES emulsion compared to that treated with PIBS latex/OTES emulsion may have a contribution from the lesser hydrophobicity of the small methyl group in the PDMS in a comparison with the isobutyl group of PIBS.

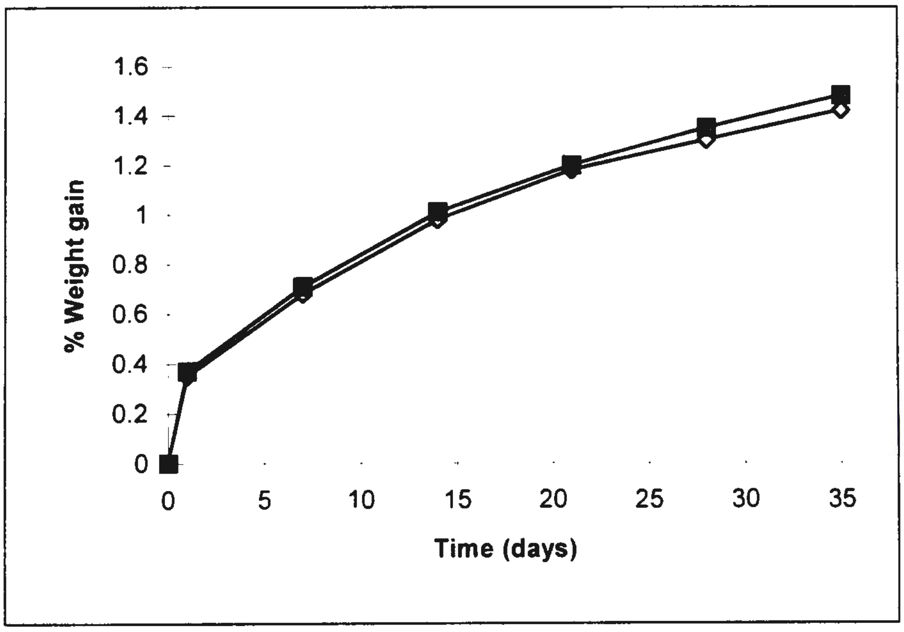


Figure 6.7. Water absorption of concrete treated with diluted emulsions

(◊) 20% PIBS latex/OTES emulsion
(□) 20% PDMS/OTES emulsion

The water absorption of the concrete treated with diluted emulsions containing 20% silane is reduced by 94% compared to untreated concrete after one day of test. This indicates that emulsions containing 20% silane are effective in protecting concrete against water ingress (Figure 6.8).

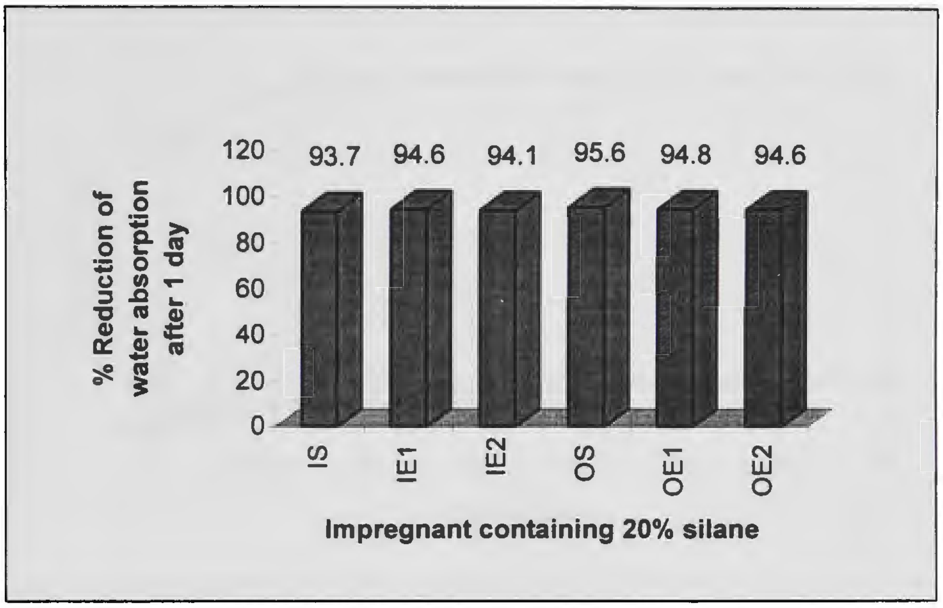


Figure 6.8. Reduction of water absorption of the treated concrete after one day test

IS = IBTES solution
IE1 = PIBS latex/IBTES emulsion
IE2 = PDMS/IBTES emulsion
OS = OTES solution
OE1 = PIBS latex/OTES emulsion
OE2 = PDMS/OTES emulsion

6.6. Alkali stability of the impregnants in the treated concrete

Cementitious substrates such as concrete are inherently alkaline in nature. The hydroxide ions (OH^-) in the pore water are able to attack and break apart some siloxane linkages (-O-Si-O-) between the silane/siloxane molecules and between the silicone and the substrate. Therefore, alkali stability of the impregnants in the treated medium is necessary for the impregnation to provide long term protection.

The relationship between the time of immersion in 10% KOH solution and the percentage weight gain of the treated and untreated concrete is shown in Figure 6.9. The alkali resistance of the emulsion impregnant in the substrate is similar to that of the silane solution impregnant in the substrate.

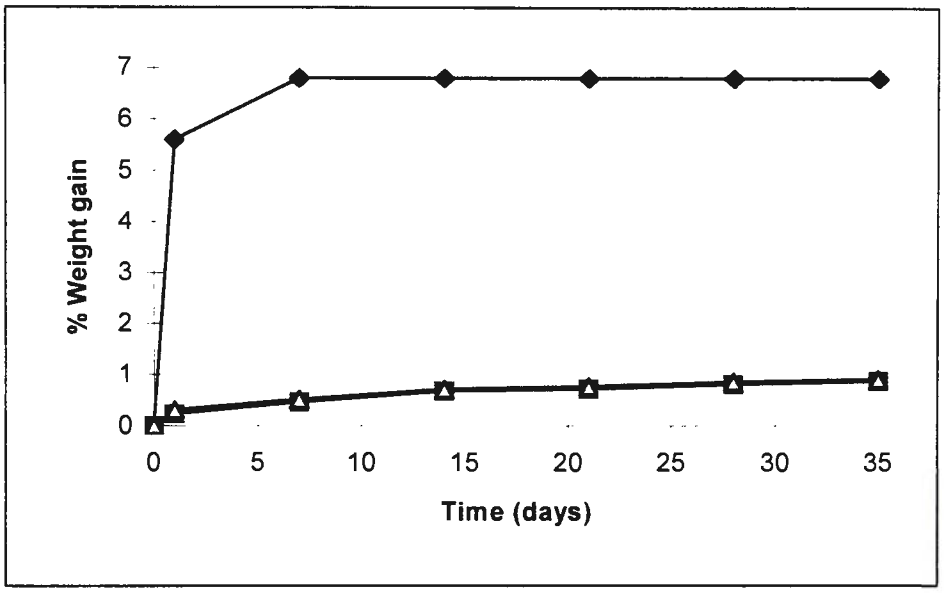


Figure 6.9. Alkali resistance of impregnated concrete

(◊) untreated concrete
(□) 40% OTES solution
(Δ) 40% PIBS latex/OTES emulsion

Figure 6.10 indicates that diluted PIBS latex/IBTES emulsion containing 20% IBTES is more alkali resistant than the hydrocarbon solution containing the same concentration of silane. This indicates that the presence of a polysiloxane in the emulsion has an improving effect on the alkali stability. The concrete treated with diluted PDMS/IBTES emulsion is less alkali resistant than that treated with diluted PIBS latex/IBTES emulsion. This may be attributed to less effective resistance to the alkali of the PDMS film with the methyl group on the treated surface. Depending on its size and shape, the alkyl group can protect the siloxane linkage (-Si-O-Si-) by blocking the entry of the hydroxide ions to the silicone atom. Therefore, the methyl group of PDMS provides less resistance to the intrusion of hydroxide ions than the isobutyl group of PIBS.

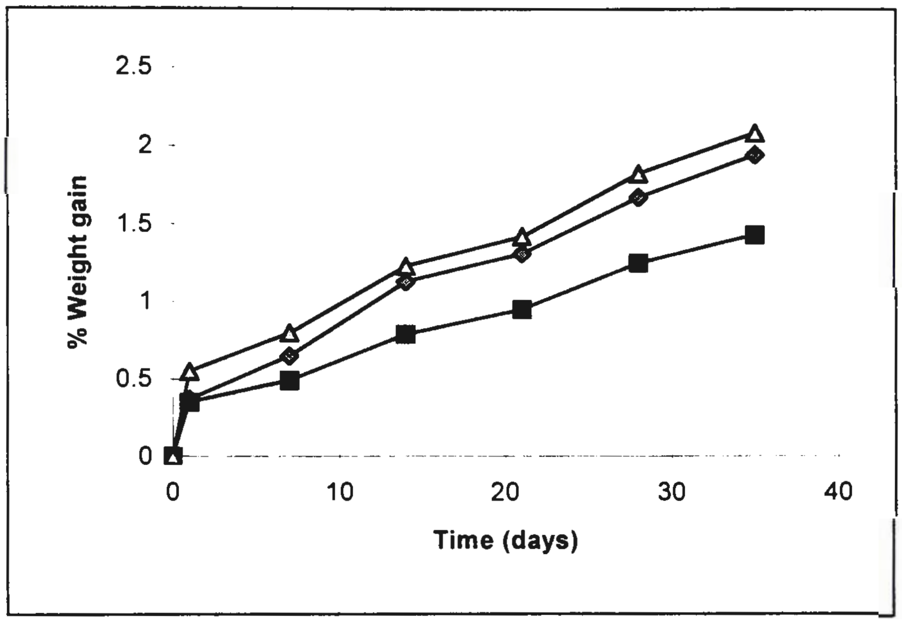


Figure 6.10. Alkali resistance of substrates treated with IBTES impregnants

(□) 20% PIBS latex/IBTES emulsion
(◊) 20% IBTES solution
(Δ) 20% PDMS/IBTES emulsion

The same trend is exhibited in the case of the concrete treated with OTES emulsions (Figure 6.11). The lower alkali resistance of the concrete treated with PIBS latex/OTES emulsion or PDMS/OTES emulsion compared to that treated with the OTES hydrocarbon solution may be attributed to the lower alkali resistance due to the isobutyl group of PIBS in PIBS latex/OTES emulsion or the methyl group of PDMS in PDMS/OTES emulsion compared to the higher alkyl group in the OTES solution.

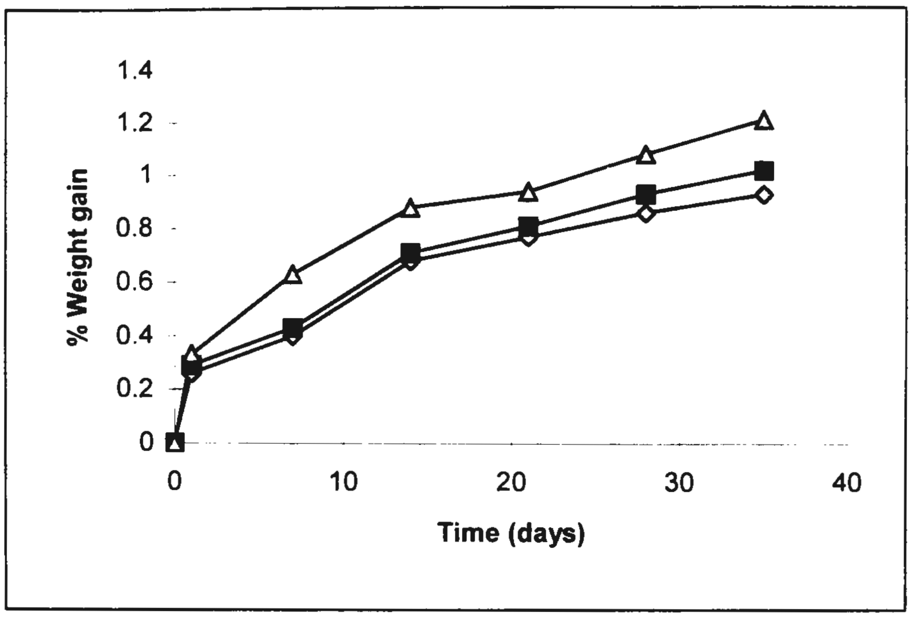


Figure 6.11. Alkali resistance of substrates treated with OTES impregnants

(◊) 20% OTES solution
(□) 20% PIBS latex/OTES emulsion
(Δ) 20% PDMS/OTES emulsion

As shown in Figure 6.12, the alkali resistance of the concrete treated with diluted PIBS latex/OTES emulsions is better than that treated with diluted PDMS/OTES emulsion. This implies that the alkali resistance due to the isobutyl group of PIBS in the emulsion is better than that due to the methyl group of the PDMS in the PDMS/OTES emulsion. Figure 6.13 shows that the alkali resistance of the concrete treated with PIBS latex/OTES emulsion is better than that treated with other emulsions. The resistance to hydroxide ions of the impregnated layer in the substrate treated with diluted PIBS latex/OTES emulsion is comparable to that treated with OTES solution containing the same silane concentration.

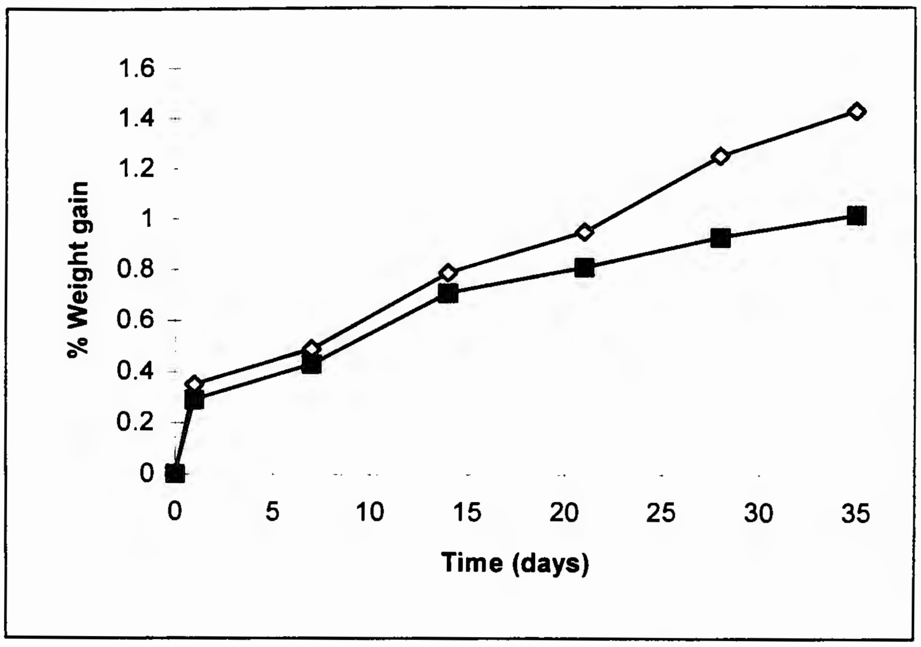


Figure 6.12. Alkali resistance of substrates treated with OTES impregnants

(□) 20% PIBS latex/OTES emulsion
(◊) 20% PDMS/OTES emulsion

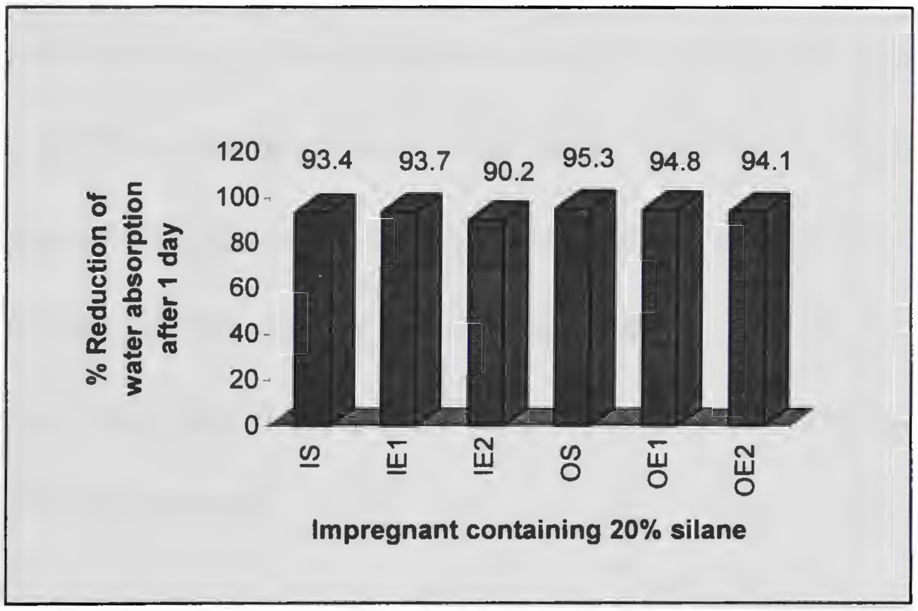


Figure 6.13. Reduction of water absorption of the treated concrete after one day sponge test in 10% KOH solution

IS = IBTES solution	OS = OTES solution
IE1 = PIBS latex/IBTES emulsion	OE1 = PIBS latex/OTES emulsion
IE2 = PDMS/IBTES emulsion	OE2 = PDMS/OTES emulsion

6.7. Chloride ion resistance of the treated concrete

The ingress of chloride ion into concrete is one of the most serious problems encountered in concrete structures. Chloride ion is considered as one of the main factors contributing to the corrosion of steel in concrete. Chloride ion, in the presence of moisture, interrupts the passivating film on the embedded steel and leads to corrosion. Tests carried out in this study were aimed at evaluating the chloride ion resistance of the concrete treated with novel emulsions.

Figure 6.14 shows the chloride ion resistance of the concrete substrates treated with IBTES solution and emulsions. Chloride ion penetrates into concrete in its hydrated form, therefore, the degree of water repellency relates to the extent of the chloride ion screening. The chloride ion resistance of the concrete substrates treated with IBTES emulsions is better than those treated with IBTES solution. The water absorption of the concrete treated with IBTES emulsions is lower than those treated with IBTES solution and thus the concrete treated with emulsions would be expected to exhibit better resistance to the chloride diffusion than those treated with IBTES solution.

The reduction of water absorption of the concrete treated with the OTES solution is greater than those treated with the OTES emulsions (Figure 6.8). Therefore, the concrete treated with the OTES solution exhibits better resistance to the chloride diffusion than those treated with OTES emulsions (Table 6.3 and

Figure 6.15). This may be attributed to the effect of the alkyl groups of the polysiloxanes in the emulsion being methyl and isobutyl on the water absorption of the treated concrete.

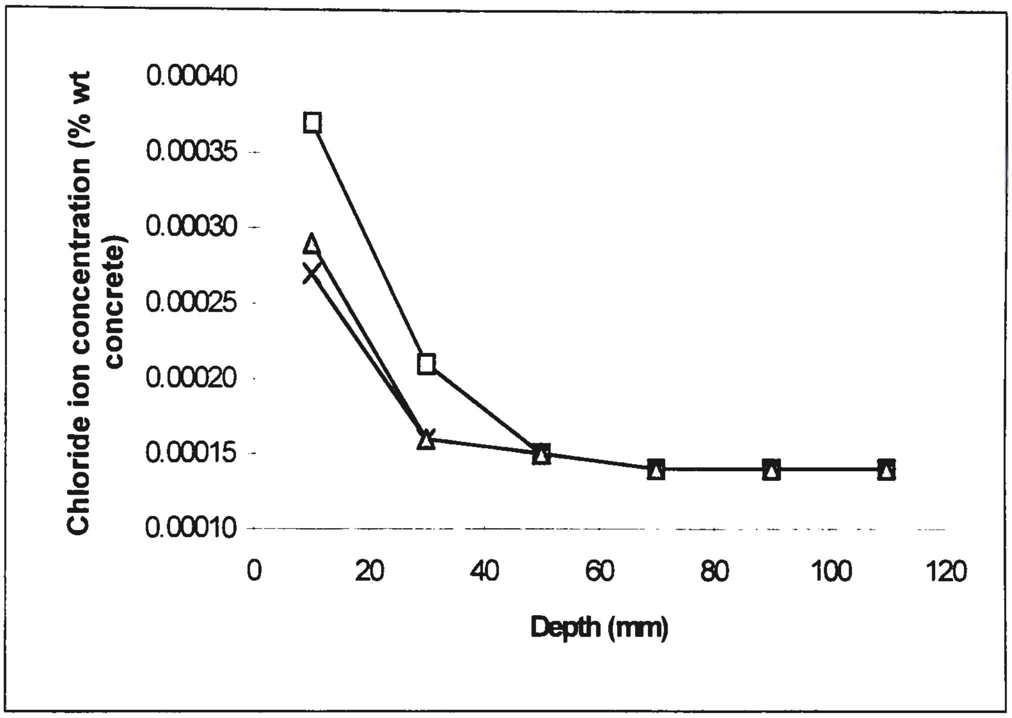


Figure 6.14. Chloride ion diffusion through concrete substrates treated with diluted IBTES impregnants containing 20% silane after 35 days test
(□) IBTES solution
(Δ) PDMS/IBTES emulsion
(×) PIBS latex/IBTES emulsion

The concentration of chloride ion of the concrete substrates treated with the silane impregnants at a depth of 0-20 mm is within the range of 1.5×10^{-4} and 4.0×10^{-4} % by weight of the concrete compared to the control. The threshold chloride concentration for the corrosion of reinforcing steel is about 3.0×10^{-2} to 5.0×10^{-2} % by weight of the concrete.[150] As the concentration of chloride in the treated concrete is very low compared to the threshold value, the treatment of the concrete with silane impregnants will effectively protect the embedded steel from chloride ion penetration from the service environment.

Impregnants with 20% silane concentration	% Cl^- reduction at the depth of 0-20 mm	% Water reduction after 35 days
IBTES solution	86.2	82.1
PDMS/IBTES emulsion	91.0	83.3
PIBS latex/IBTES emulsion	92.0	83.8
OTES solution	98.1	85.4
PDMS/OTES emulsion	95.3	84.4
PIBS latex/OTES emulsion	96.5	84.8

Table 6.3. The relationship between chloride ion diffusion and the water absorption of the treated concrete after 35 days test

The percentage chloride reduction at different depths below the treated concrete surface is shown in Table 6.4. At a depth of 0-20 mm below the treated surface, all the impregnants have the ability to reduce by more than 90% the chloride ingress into the treated concrete with the exception of the IBTES solution.

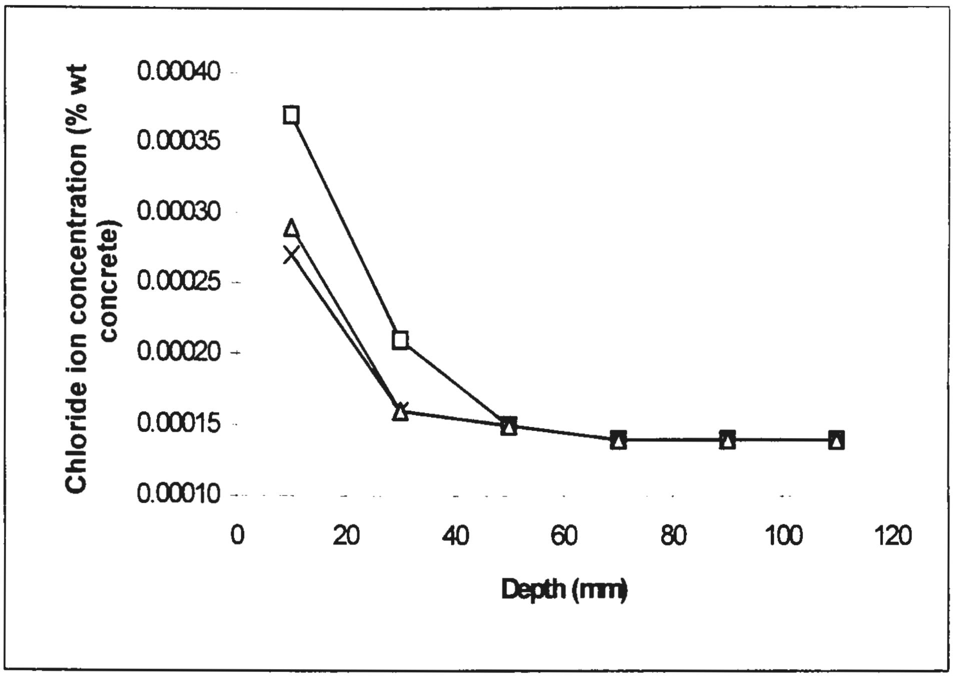


Figure 6.15. Chloride ion diffusion through concrete substrates treated with diluted OTES impregnants containing 20% silane after 35 days test

(□) PDMS/OTES emulsion
(Δ) PIBS latex/OTES emulsion
(×) OTES solution

Impregnants with 20% silane concentration	% Cl⁻ reduction at the depth of 20 mm	% Cl⁻ reduction at the depth of 40 mm
IBTES solution	86.1	95.4
PDMS/IBTES emulsion	91.0	97.6
PIBS latex/IBTES emulsion	92.0	98.7
OTES solution	98.1	99.5
PDMS/OTES emulsion	95.3	98.7
PIBS latex/OTES emulsion	96.5	98.7

Table 6.4. The relative reduction of chloride ion in the treated concrete at different depths below the treated surface

6.8. The effect of UV radiation on impregnants in the treated concrete

Concrete is exposed to weathering influences and therefore the durability of the impregnants is also governed by their resistance to the destructive effect of UV.

The visual appearance of the treated surface before and after 1500 hours of UV and condensation testing remained similar. The beading effect of all the treated substrates was significantly decreased after the test as shown in Table 6.5. This indicates that the destructive effect of UV on the polysiloxane at the surface of the treated substrate is unavoidable.

Impregnants	Beading effect before test	Beading effect after test
IBTES solution	3	5
PIBS latex/IBTES emulsion	3	5
PDMS/IBTES emulsion	2	5
OTES solution	2	5
PIBS latex/OTES emulsion	2	5
PDMS/OTES emulsion	1	5

Table 6.5. The beading effect of the treated concrete before and after the UV and condensation weathering test

After 1500 hours of the UV and condensation weathering test, the concrete samples treated with silane impregnants are still capable of reducing by greater than 90% the water ingress compared to the untreated concrete (Figure 6.16). This implies that the UV only has an effect on the polysiloxane layer at the very surface of the treated substrate, but the hydrophobic polysiloxane layer inside the treated concrete is unaffected by the destructive effect of the UV.

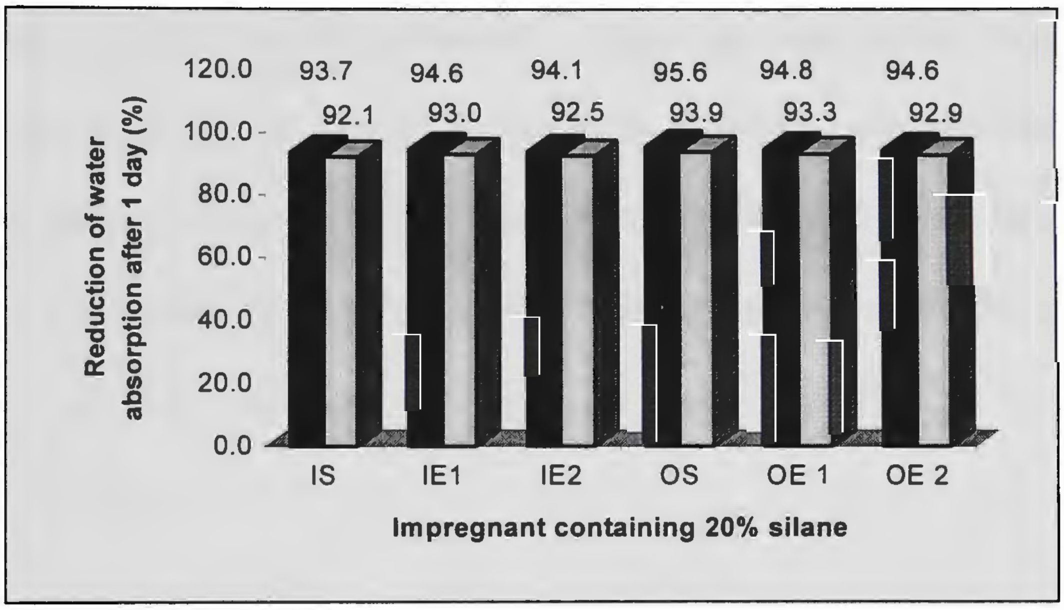


Figure 6.16. Reduction of water absorption of the treated concrete before (■) and after (□) 1500 hours UV and condensation weathering test

IS = IBTES solution
IE1 = PIBS latex/IBTES emulsion
IE2 = PDMS/IBTES emulsion
OS = OTES solution
OE1 = PIBS latex/OTES emulsion
OE2 = PDMS/OTES emulsion

6.9. Efflorescence resistance of the treated concrete

Efflorescence is a phenomenon in which salt emerges to the concrete surface causing white surface deposits. As water moves through a concrete structure, it dissolves soluble salts and when it reaches the surface the water evaporates leaving solid salt efflorescence on the concrete surface. The efflorescence resistance test on concrete substrates treated with silane impregnants was conducted over 14 days in a 10% aqueous sodium sulphate solution (ξ 3.4.8). Test results showed that there was no efflorescence on the treated surfaces. This indicated that the impregnation of concrete with silane solution or silane/siloxane emulsions interrupts the transport of salts at the boundary between the impregnated and unimpregnated areas. Water can only move from the unimpregnated area to the concrete surface in the form of vapour, and therefore, it cannot carry salts with it. As a result, salts are deposited at the boundary between impregnated and unimpregnated areas and cannot reach the treated surface.

CHAPTER SEVEN

Conclusions

Novel silane/siloxane emulsions in which alkylalkoxysilanes were the base material have been developed in this research.

It was found that a stable emulsion could be produced with a composition containing an alkylalkoxysilane with a polyisobutylsiloxane (PIBS) latex which was prepared by the emulsion polymerisation of commercial isobutyltrimethoxysilane. By substituting polyisobutylsiloxane latex with a commercial silicone fluid, another stable emulsion was formed with an amine soap as the surfactant. The optimum concentration of alkylalkoxysilane in the novel emulsions was 40% by weight. The concentration of siloxane was varied depending on the structure, molecular weight of the siloxane, the type and concentration of the emulsifier. In PIBS latex/silane emulsions, the siloxane was PIBS latex in which the molecular weight of a cross-linked PIBS was in the range between 800 and 4000. The preferred concentration of PIBS in PIBS latex/silane emulsions was about 18% by weight. No further addition of surfactant was necessary to make the emulsion than that already present in the PIBS latex. The preferred concentration of a polydimethylsiloxane (PDMS) with a molecular weight of 13,500 in PDMS/silane emulsions was 10% by weight. The desired surfactant for PDMS/silane emulsions was an amine soap with the concentration being more than 1% by weight.

Characterisation of the novel emulsions showed that the polysiloxane played an important role in the formation and the stability of the novel silane/siloxane emulsions. The polysiloxane increased the stability of the emulsions through adsorption at the water-oil interface. The use of an organopolysiloxane in the preparation of silane/siloxane emulsions also made the determination of the optimum HLB value at which the alkylalkoxysilane can be emulsified unnecessary and the emulsification process of silanes became more practical. The polysiloxane improved the beading effect and the water repellency of the treated concrete when compared to the silane solutions. This was due to the formation of an hydrophobic film on the treated surface. The polysiloxane also had a great influence on the viscosity of the novel emulsions.

The emulsion polymerisation of isobutyltrimethoxysilane was a complex process in which surfactant and the silanol monomer/water ratio played an important role in the formation and the stability of the polyisobutylsiloxane latex. These factors also influenced the stability and the performance of the final polyisobutylsiloxane latex/silane emulsions. The size of the polyisobutylsiloxane latex particles and the molecular weight of the polyisobutylsiloxane were controlled effectively by the temperature of the reaction and the suitable concentration of surfactant. This production of a suitable size and molecular weight polysiloxane for incorporation in the emulsion had a beneficial effect on film formation when the emulsion was used to treat concrete substrates.

The study of the viscosity of the novel emulsions showed that the novel emulsions were suitable for impregnating techniques such as spraying, rolling or brushing. The shear thinning behaviour of concentrated emulsions and the Newtonian behaviour of the diluted emulsions would have a beneficial effect on an impregnation operation.

The novel emulsions developed by this research were very stable and had a long shelf life. They were storable as concentrates for a long period of time. The efficacy of the novel emulsions was not affected by long term storage. The novel emulsions maintained a high level of the original silane due to the choice of silanes with hydrolytic stability.

It was found that the polyisobutylsiloxane latex/silane emulsions performed marginally better than polydimethylsiloxane/silane emulsions in terms of water repellency and long term protection of the treated concrete. This may be attributed to the large isobutyl group of the polyisobutylsiloxane compared to the small methyl group of polydimethylsiloxane. Although the penetration depth of the octyltriethoxysilane emulsions was lower than that of the isobutyltriethoxysilane emulsions, the performance of the octyltriethoxysilane emulsions in general, were much better than the performance of the isobutyltriethoxysilane emulsions. This may be attributed to the very hydrophobic octyl group of the octyltriethoxysilane and a high resistance to hydroxide ion attack due to the steric effect of the octyl group and the insolubility and hydrophobicity of octyl hydrolysis products.

Diluted emulsions which contained only 20% silane were found to be effective for concrete protection. The performance of the diluted emulsions in terms of water resistance, alkali stability, UV resistance, efflorescence resistance and chloride resistance was comparable to organic solvent-based products containing the same concentration of silane.

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ABBREVIATIONS

ABSA	Alkylbenzenesulphonic acid
ASTM	American Society for Testing and Materials (Standard method)
BS	British Standard
CP/MAS	Cross polarisation and magic-angle spinning
DIN	Deutsche Institut für Normung (German standard)
ELSD	Evaporative light scattering detector
GC-MS	Gas chromatograph-mass selective detector
GPC	Gel permeation chromatography
HLB	Hydrophilic and lipophilic balance
IBST	Isobutylsilanetriol
IBTES	Isobutyltriethoxysilane
IBTMS	Isobutyltrimethoxysilane
MTMS	Methyltrimethoxysilane
MWD	Molecular weight distribution
OTMS	Octyltrimethoxysilane
OTES	Octyltriethoxysilane
PDMS	Polydimethylsiloxane
PIBS	Polyisobutylsiloxane
PSD	Particle size distribution
SDBS	Sodium dodecylbenzenesulphonate
SSA	Specific surface area
THF	Tetrahydrofuran