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SYNTHESIS AND ANTIBACTERIAL ACTIVITY OF WATERBORNE POLYURETHANE CONTAINING QUATERNIZED SILICA

Mister Sumet Lertpanyachokchai

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By	Mister Sumet Lertpanyachokchai
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Thesis Advisor	Associate Professor Supawan Tantayanon, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

………………………………………….……. Thesis Advisor
(Associate Professor Supawan Tantayanon, Ph.D.)

……………………………………………….. Examiner
(Asistant Professor Warinthon Chavasiri, Ph.D.)

……………………………………………….. External Examiner
(Warayuth Sajomsang, Ph.D.)

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ซิลิกาถูกเตรียมจากโซเดียมซิลิเกตกับกรดอะซิติก บริเวณพื้นผิวจะถูกปรับปรุงด้วยการควบคู่กับ 3-อะมิโนโพรพิลไตรเอทท็อกซี่ไซเลน (เอพีทีอีเอส) และต่อมาทำปฏิกิริยากับ 3-คลอโร-2-ไฮดรอกซีเมทิลแอมโมเนียมคลอไรด์ ทำให้เกิดเป็นควอเทอร์ไนซ์ซิลิกา พอลิยูรีเทนพลิพอลิเมอร์ถูกสังเคราะห์จากพอลิเอสเทอร์พอลิออล, ไอโซโฟโรนไดไอโซไซยาเนตและกรดไดเมทิลออลโพรไพโอนิก เอพีทีอีเอสถูกเติมลงในพอลิยูรีเทนพลีพอลิเมอร์ก่อนเติมควอเทอร์ไนซ์ซิลิกาโดยควอเทอร์ไนซ์ซิลิกามีการใช้อัตราส่วนต่างๆ พอลิยูรีเทนชนิดน้ำถูกผลิตโดยกระบวนการเซลฟ์ -อิมัลสิฟิเคชัน ซึ่งวัฏภาคน้ำมันจะประกอบด้วยไอโซไซยาเนตปลายสายโซ่ของพลีพอลิเมอร์, ตัวเร่งเป็นไดบิวทิวทิน ไดลอเรท, สารเชื่อมขวางเป็นไตรเอทิล เอมีน (ทีอีเอ)และสารเพิ่มสายโซ่เป็นเอทิลลีนไดเอมีน (อีดีเอ) แล้วนำไปกระจายตัวในวัฏภาคน้ำ ทุกผลิตภัณฑ์ถูกพิสูจน์เอกลักษณ์ด้วยฟูเรียทรานฟอร์มอินฟราเรดสเปกโทรสโกปี (เอฟทีไออาร์), ^{29}ซิลิกอนเอ็นเอ็มอาร์และทีอีเอ็ม วิธีการทดสอบฤทธิ์ยับยั้งแบคทีเรีย (*Escherichia coli*) และ (*Staphylococcus aureus*) ของพอลิยูรีเทนชนิดน้ำทีมีควอเทอร์ไนซ์ซิลิกาไฮบริดใช้แบบวิธีการแขวนลอย พอลิยูรีเทนชนิดน้ำทีมีควอเทอร์ไนซ์ซิลิกาไฮบริดที่เตรียมได้สามารถแสดงสมบัติที่ดีเชิงความร้อนและสมบัติทางกล

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Silica was prepared from sodium silicate by reacting with acetic acid. Its surface was firstly modified by coupling with 3-aminopropyltriethoxysilane (APTES) and further reacted with 3-chloro-2-hydroxyltrimethyl ammonium chloride to obtain quaternized silica. Polyurethane prepolymer was then generated from polyester polyol, isophoronediisocyanate and dimethylolpropionic acid. APTES was added to polyurethane prepolymer prior to the addition of the as-prepared quaternized silica. The quaternized silica content was varied. Waterborne polyurethane was then produced by self-emulsification method in which an oil phase containing NCO-terminated prepolymer, the catalyst dibutyltin dilaurate, the crosslinking agent triethyl amine (TEA) and the chain extender ethylene diamine (EDA), was dispersed in the water phase. All the products were characterized by FTIR, ^{13}C NMR and ^{29}Si NMR spectroscopy and TEM. The antibacterial activity of quaternized silica and water polyurethane containing quaternized silica against *Escherichia coli* and *Staphylococcus aureus* was examined by the suspension quantitative method. The waterborne polyurethane containing quaternized silica showed good thermal stability and mechanical property.

Field of study : Petrochemistry and Polymer Science Student's Signature……………………
Academic Year : 2009 Advisor's Signature…………………..

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LIST OF ABBREVIATION

^{o}C	degree Celsius
g	gram
h	hour
µm	micrometre
mg	milligram
mL	millilitre
mL/ min	millilitre per minute
min	minute
M	molarity
mol L^{-1}	mol per litre
nm	nanometre
N	normal
cm^{-1}	wave number
wt	weight
PU	Polyurethane

CHAPTER I

INTRODUCTION

In recent years, organic–inorganic hybrid composites based on organic polymer and inorganic materials show an important role in modifying the formation polyurethane. The waterborne polyurethane hybrid nano composites have attracted good interest of researchers, because they often show remarkable improvement in material properties when compared with pure waterborne polyurethane. These improvements include high modul, higher mechanical strength, increased tensile strength and heat resistance. On the other hand, water dispersions, latexes or emulsions of polyurethane elastomers or coatings permit the application of polyurethanes hybrid nano composites from an aqueous medium. Waterborne polyurethane are nontoxic, non-flammable, and do not pollute the air, thus rendering these systems safe with regard to the environment [1].

Polyurethane coatings were originally defined as products made from polyols and polyisocyanate but now a broader definition is used that includes all systems based on a polyisocyanate whether the reaction is with a polyol, a polyamine or with water. Consequently a polyurethane coating may contain urethane, urea, allophanate and biuret linkages. Since their introduction in the 1950s polyurethane coatings have grown rapidly because of the highly versatile chemistry and the excellent properties including toughness and abrasion resistance, combined with flexibility, chemical resistance and good adhesion [2].

The polyurethanes coating industry, comsumption of thermoplastic polyurethanes (TPUs) is estimated at 357,100 tonnes in 2004, with Asia accounting for just over 50% of demand, Europe a further 27% and the Americas the remainder. The main application areas for industrial coatings are automotive, aircraft, electrical insulation, electronics, textile, leather, wood products, coil coating, applications for coatings are the protection of metalwork and sealing floors and roofs whilst the decorative architectural applications mainly involve wood varnishes and pigmented enamels. Speciality/maintenance coatings are used mainly in automotive refinish, anti-corrosion, flooring, roofing and decking [3].

Inoraganic silica exhibits a number of beneficial properties such as transparency, surface hardness, heat resistance, and high mechnical properties. In almost all cases, the benefits of smaller sized particles can only be realized if the particles are well dispersed, either in a solvent or in other solid matrices. However, the complex surface chemistry of silica tends to destabilize suspensions, especially for small particles which have a very high specific surface area. While surface modification has been used extensively for improving colloidal stability, and various silanes have been used for such a purpose on colloidal silica, some studies modified the surface of large colloidal particles [4].

In addition, quaternary ammonium compounds belong to the group of compounds, which exhibit high antibacterial activity, They are widely used in many of domains such as environmental disinfection, equipment surfaces and disinfection in hospitals. These compounds seem to be safer than chemically active disinfectants such as chlorine and glutaraldehyde. However, since the irritant and cytotoxic effects of these compounds on human cells tissues such as keratinocytes, fibroblasts, sornea and respiration mucosa have been shown previously, the improvement of quaternary ammonium compounds is necessary, not only for their antibacterial activity but also for human cells safety. To overcome these problems, anchoring the quaternary ammonium compounds to a polymer backbone by covalent might be promising in developing materials which would have antibacterial activity by themselves [5].

Accordingly, it will be useful if polyurethane, silica and 3-chloro-2-hydroxypropyl trimethylammonium chloride (Quat-188) can be synthesized for coating application. This will provide not only good coating vehicle but also improve mechnical property and antibacterial activity of coating.

1.1 Objectives of Research

1. To synthesize quaternized silica and waterborne polyurethane containing quaternized silica.
2. To study mechanical property and antibacterial activity of waterborne polyurethane containing quaternized silica.

1.2 Scope of Research

1. To synthesize quaternized silica from sodium silicate.
2. To synthesize waterborne polyurethane containing quaternized silica by sol-gel process.
3. To characterize waterborne polyurethane containing quaternized silica by FTIR and Solid State NMR technique.
4. To synthesis waterborne polyurethane containing quaternized silica inhibited the growth of *E.coli*. and *S.aureus.*
5. To study mechanical properties of waterborne polyurethane containing quaternized silica.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Sodium silicate

Sodium silicate, also called water glass or soluble glass, is any one of several compounds containing sodium oxide, Na_2O, and silica, Si_2O, or a mixture of sodium silicates varying ratios of SiO_2 to Na_2O, solids contents, and viscosity. Traditionally, sodium silicates are classified according to the acid from which they are derived as Orthosilicate Na_4SiO_4, Metasilicate Na_2SiO_3, Disilicate $Na_2Si_2O_5$, Tetrasilicate $Na_2Si_4O_9$. They are also classified by an X-ray diffraction method according to their crystalline structure. All these compounds are colorless, transparent, glasslike substance available commercially as a powder or as a transparent, viscous solution in water. They can be dissolved in water to form a syrupy liquid. Some forms are slightly soluble, and some are almost insoluble; they are best dissolved by heating with water under pressure. The solutions are strongly alkaline. They are produced chiefly by fusing sand and sodium carbonate in various proportions. The use of sodium silicates is as a raw material for making silica gel. Also used in detergent; as a cement for glass, pottery, and stoneware; for fireproofing paper, wood, cement, and other substances; for fixing pigments in paintings and cloth printing; and for preserving eggs [6].

Applications

- Silica gel production
- Builder or anti-soil-redeposition agent for detergent
- Peroxide stabilizer in bleaching for textile and pulp
- Solubilizer in ink, flux binder for welding rods
- Deflocculant for ceramic
- Buffer
- Fireproofing paper catalysts

- Water treatment
- Concrete hardner and acid-proof
- Petroleum processing by emulsion breaking and corrosion prevention
- Timber treatment

2.1.2 Silica aerogels

Silica aerogels are extremely porous materials with highly crosslinked network of silica particles, consisting of less than 10% silica and more than 90% air. Typically, they exhibit low density (0.03 g/cm3), low thermal conductivity (0.05 W/m K), low refractive index (1.01 to 1.1), large surface area (1600 m^2/g) and high hydrophobicity. These extraordinary properties of silica aerogels make them as a unique material in many fields of applications: Cerenkov radiation detectors in nuclear reactors, filters, membranes, collectors for micrometeorites in space and as a liquid rocket propellants, catalyst supports, thermal super-insulators for solar ponds, hot water system and in refrigerators. and so on.

Generally silica aerogels are produced by hydrolysis and condensation of silicon alkoxides like TMOS or TEOS in the presence of an acidic or basic catalyst followed by supercritical drying in an autoclave. Since, various groups have prepared monolithic and transparent silica aerogels applying the same method. However, this method of preparation of aerogels in an autoclave is very risky and expensive. Because the drying occurs at high temperature and pressure with evacuation of highly flammable gases and the chemicals used are hazardous for health and costly. Hence, for commercialization, it is necessary to produce silica aerogels using cheap inorganic precursor and drying the gels at ambient pressure. Therefore, for easy availability we prepared the silica aerogels using sodium silicate precursor and dried the gels at ambient pressure. So, to produce low density aerogels, we tried various acids as catalyst for the preparation of silica aerogels [7,8].

2.1.3 Quaternary ammonium salt

Quaternary ammonium cations, also known as quats, are positively charged polyatomic ions of the structure NR_4^+, R being an alkyl group. Unlike the ammonium ion (NH_4^+) and the primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution. Quaternary ammonium salts or quaternary ammonium compounds (called quaternary amines in oilfield parlance) are salts of quaternary ammonium cations with an anion. As antimicrobials certain quaternary ammonium compounds, especially those containing long alkyl chains, are used as antimicrobials and disinfectants. Examples are benzalkonium chloride, benzethonium chloride, methylbenzethonium chloride, cetalkonium chloride, cetylpyridinium chloride, cetrimonium, cetrimide, dofanium chloride, tetraethylammonium bromide, didecyldimethylammonium chloride and domiphen bromide. Also good against fungi, amoeba, and enveloped viruses. Quats act by disrupting the cell membrane. Quaternary ammonium compounds are lethal to a wide variety of organisms except endospores, Mycobacterium tuberculosis, non-enveloped viruses, and Pseudomonas spp. (some Pseudomonas spp. can even grow in solutions of quats, subsisting on them).

In contrast to phenolics, quaternary ammonium compounds are not very effective in the presence of organic compounds. Yet quats are very effective in combination with phenols. Quaternary ammonium compoundss are deactivated by soaps, other anionic detergents, and cotton fibers. Also, they are not recommended for use in hard water. Effective levels are at 200 ppm. They are effective at temperatures up to 212 ºF.

Recently, much attention has been directed to specialty polymers of the most useful materials. Quaternary ammonium salts (QAS) possessing at least one alkyl substituent are able to kill microorganism such as bacteria and fungi by interacting with the cell membrane [9, 10, 11].

2.1.4 Bacteria

2.1.4.1 Morphology and ultrastructure

The size, shape and arrangement of bacteria and other microbes is the result of their genes and is defining characteristic called morphology. Bacteria come in a bewildering and exciting variety of size and shapes. The most common bacterial shapes are rods (bacill) and spheres (cocci). Whin each of these groups is hundreds of unique variations. Rods may be long, short, thick, or thin and have rounded or pointed ends, thicker at one end than the other, etc. Cocci may be large, small, or oval shaped to various degrees. Spiral shaped bacteria may be fat, thin, loose spirals or very tight spirals

2.1.4.2 Gram staining

Bacteria can be classified to two major groups, Gram-positive and Gram-negative, based on the Gram staining reaction shown in Figure 2.1. Differences in cell wall structure and composition account for the differential Gram reaction.

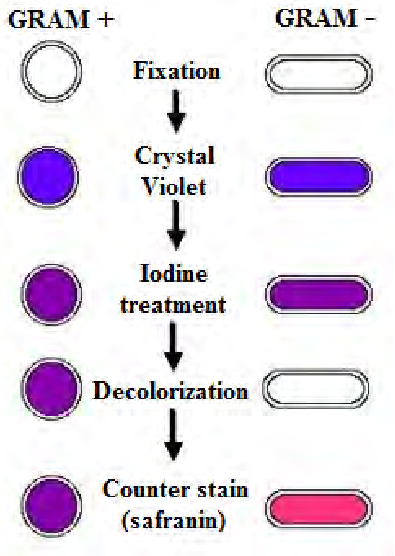


Figure 2.1. Determination of type of bacteria based on Gram staining reaction

2.1.4.3 Cell walls of bacteria

The fundamental differences in in ultrastructure of the cell wall are responsible for the reaction (+ or -) of bacteria toward the Gram stain. In both types of cells, the cytoplasmic membrane is surrounded and supported by a cell wall, which provides strength, rigidity and shape. The cross sections of these structures are shown in Figure 2.2.

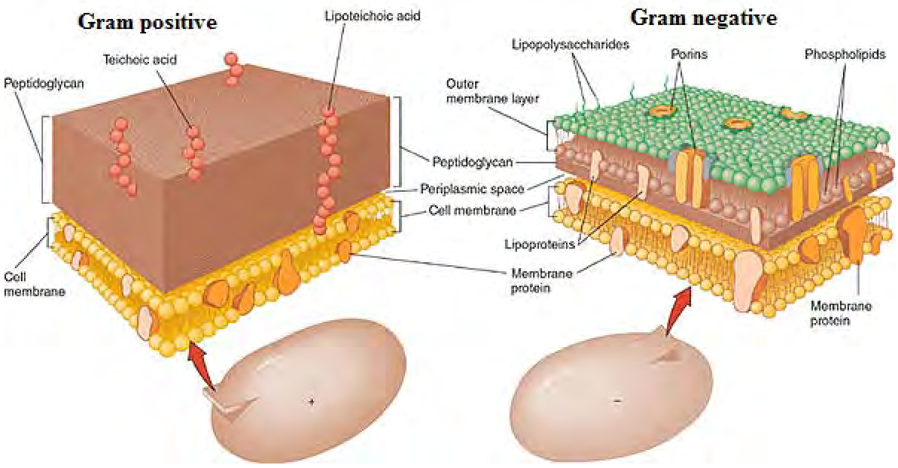


Figure 2.2. The cross sections of Gram-positive and Gram-negative bacteria cell walls

In this study, Gram-positive (i.e., *Staphylococcus aureus*) and Gram-negative (i.e., *Escherichia coli*) were used. Gram-positive bacteria tend to have a loose cell wall, while Gram-negative bacteria have an outer membrane structure in the cell wall forming an additional barrier for foreign molecules as shown in Figure 2.3

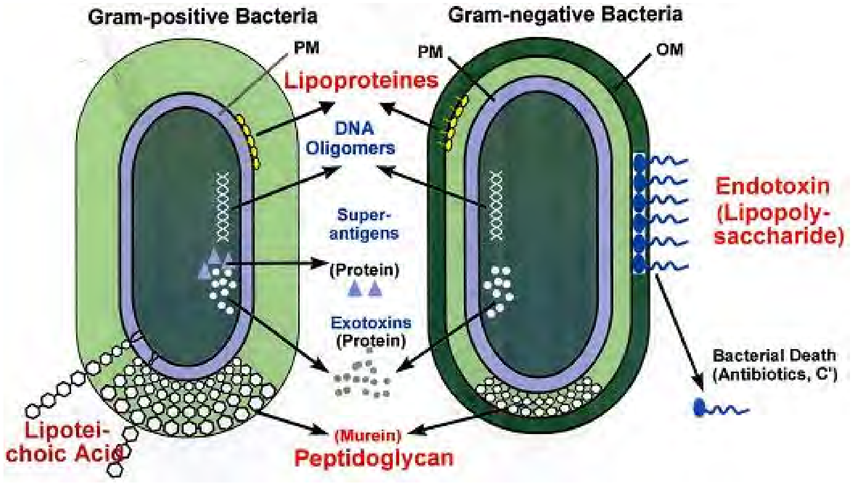


Figure 2.3. Cell wall structures of Gram-positive and Gram-negative

2.1.4.4 Gram-positive bacteria

The wall, which lines outside the cytoplasmic membrane, is usually between 15 and 50 nm thick. The major part of the Gram-positive wall is a large polymer comprising two covalently linked components. One of these components, forming at least 50% of the wall mass, is peptidoglycan. Its cross-linked structure provides a tough, fibrous fabric giving strength and shape to the cell and enabling it to withstand a high internal osmotic pressure. Attached to the peptidoglycan is an acidic polymer, such as teichoic acid, lipoteichoic acid and teichuronic acid, which differs from species to species. The acidic character of the polymer attached to the peptidoglycan ensures that the cell surface is strongly polar and carries an negative charge. This may influence the passage of ions, particularly magnesium ion and possible ionized drugs, into the cell. Other components are protein often present to the extent of 5-10%, and protein of *Staphylococcus aureus* is apparently linked covalently to peptidoglycan. The structure of cell wall Gram-positive bacteria is shown in Figure 2.4

2.1.4.5 Gram-negative bacteria

The Gram-negative wall is for more complex. Wide-ranging studies of its structure have been concentrated on *Escherichia coli* in particular. The diagram in

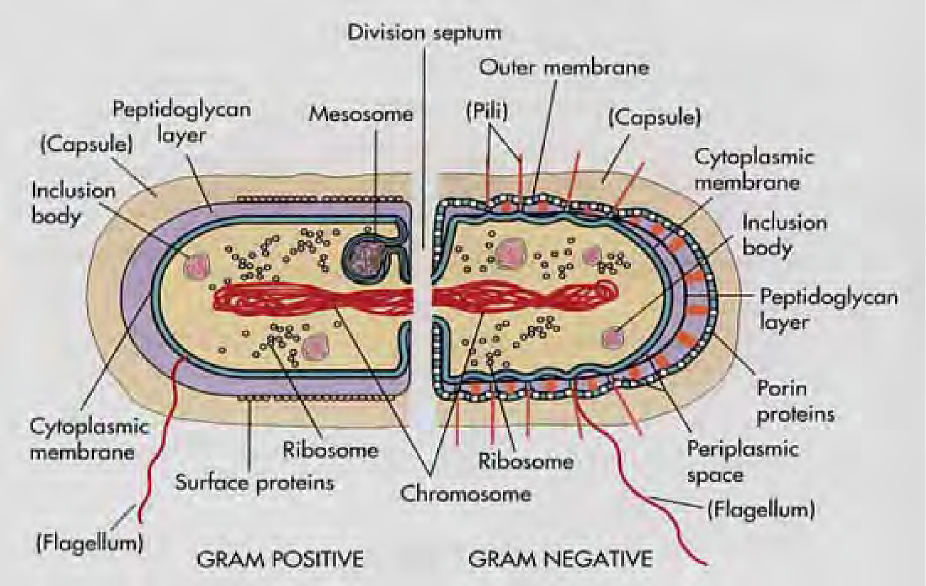


Figure 2.4. The arrangement of the cell envelope of both Gram-positive and Gram-negative bacteria.

Illustrates the general arrangement of the components of the Gram-negative cell envelope, which includes the cytoplasmic membrane as well as the cell wall. When cells of *Escherichia coli* are fixed, stained with suitable metal salts, sectioned and examined by electron microscopy, the cytoplasmic membrane is readily identified by its ‘sandwich’ appearance of two electron-dense layer separated by a lighter space. The electron-dense layer, about 2 nm thick, immediately outside the periplasm represents the peptidoglycan component of the wall. It is much thinner than in Gram-positive bacteria and may constitute only 5 to 10% of the wall mass.

The outer regions of the Gram-negative cell wall have been the most difficult to characterized. The various components together form a structure 6-10 nm thick, called the outer membrane. Like the cytoplasmic membrane it is basically a lipid bilayer (giving rise to the two outer most electron-dense bands), hydrophobic in the interior with hydrophilic groups at the outer surfaces. It also has protein components which penetrate the layer partly or completely and form the membrane. Despite these broad structural similarities, the outer membrane differs widely in composition and function from the cytoplasmic membrane. Its main constituents are lipopolysaccharide, phospholipids, fatty acids and proteins. The phospholipids, mainly phosphatidylethanolamine and phosphatidylglycerol, resemble those in the cytoplasmic membrane. The structure of the lipoloysacharide is complex and varies considerably from one bacterial strain to another. The molecule has three parts. The core is built from 3-deoxy-*D*-manno-octulosonic acid (KDO), hexoses, heptoses, ethanolamine and phosphoric acid as structural components. The three KDO residues contribute a structural unit which stongly binds the divalent ions of magnesium and calcium, an important feature stabilizing the membrane. Removal of these ions by chelting agents leads to release of some of the lipopolysaccharide into the medium; at the same time the membrane becomes permeable to compounds that would otherwise be excluded. The core polysaccharide is linked to the antigenic side chain, a polysaccharide which can very greatly from one strain to another even with in the same bacterial species. Usually it comprises about 30 sugar units, although these can vary both in number and in structure. It forms the outer most layer of the cell and is the main source of its antigenic characteristic. At the opposite end, the core of the lipopolysaccharide is attached to a moiety known as lipid A which can be hydrolysed to glucosamine, long-chain fatty acids, phosphate and ethanolamine. The fatty acid chains of lipid A, along with those of the phospholipids, align themselves to form the hydrophobic interior of the membrane. The out membrane is therefore asymmetric, with lipopolysaccharide exclusively on the outer surface and phospholipid mainly on the inner surface [12].

2.1.5 Types of Polyurethanes

In all of these applications, environmental issues ate becoming increasingly important as customers ate demanding reduced atmospheric pollutants, volatile organic compounds and hazardous air pollutants, as part of clean air regulations and desires. Polyurethane systems are already being widely adopted for these reasons, examples being moisture-curing systems with no added solvent and reactive hot-melts. In addition to solvent restrictions, higher energy efficiency, lower cure temperatures, faster curing and better material utilisation thinner films, and reduced material waste ate increasingly important. Many of the new developments in binders, adhesives and coatings are in these areas. A brief qualitative comparison of the main routes to environmentally-friendly polyurethane systems is given in Table 2.1.

Polyurethane coatings were originally defined as products made from polyisocyanates and polyols but now a broader definition is used that includes all systems based on a polyisocyanate whether the reaction is with a polyol, a polyamine or with water. Consequently a polyurethane coating may contain urethane, urea, allophanate and biuret linkages. Since their introduction in the 1950s polyurethane coatings have grown rapidly because of the highly versatile chemistry and the excellent properties including toughness and abrasion resistance, combined with flexibility, chemical resistance and good adhesion

The polyurethanes coating industry, a global market of around 1.4 million tonnes in 2000, can be divided into three broad market segments, which are industrial products (44 percent), construction and architectural (36 percent) and speciality/maintenance (20 percent). The main application areas for industrial coatings are automotive, aircraft, electrical insulation, electronics, textile, leather, wood products, coil coating, applications for coatings are the protection of metalwork and sealing floors and roofs whilst the decorative architectural applications mainly involve wood varnishes and pigmented enamels. Speciality/maintenance coatings are used mainly in automotive refinish, anti-corrosion, flooring, roofing and decking.

Table 2.1 Environmental impact of systems

System type	Advantages	Disadvantages
Solvent-borne (one- and two-component)	very high performance	solvent emissions
Solvent-borne high solids	reduced emissions Conventional equipment	Can be difficult to apply without defects Lower molecular weight/functionality hence poorer properties in general
Solvent-free moisture cure	Good performance (cross-linked network) 1K, robust cure No solvent	Cure depends on water availbility Bubble formation
Water-borne (one-component)	Much reduced emissions One-pot system	Need cross-linking Some quality problems (wetting, water sentivity)
Water-borne (two-component)	Much reduced emissions Can give high quality coating	Some quality problems (wetting, water sensitivity, NCO Index) Limited use
Powder/hot melts	No emissions Powder over spray can be recycled	Thick layers High curing temperature
radiation-cured	No emissions,Energy efficient	Capital cost of equipment Not suitable for all shapes

There are four broad types of polyurethane technology used in the coating industry, the first three of which are reactive systems with the fourth category covering all systems with no isocyanate reaction during final application:

- Two-component systems consisting of a polyisocyanate and a polyol or polyamine that are mixed just prior to application with cure generally taking place at ambient temperature(53 percent).
- Oven-curing polyurethanes use similar materials to the first category except that a blocked isocyanate is used to provide a storage stable one-pack mix with the polyol or polyamine; the isocyanate is then de-blocked

at the stoving temperature and reacts. This includes powder coating (10 percent).

- Moisture-cure polyurethanes are one-component, high molecular weight, low free-isocyanate content prepolymers that cure by the reaction with moisture from the environment to from urea linkages (4 percent).
- Non-isocyanate reactive systems, such as thermoplastic polyurethane-based lacquers, aqueous polyurethane dispersions, urethane oil and alkyds, and radiation-cured polyurethane already containing urethane or urea linkages and where there are no further isocyanated reactions during application (33 percent).

The reaction polyurethane coatings ate generally cross-linked due either to branched polyols and/or isocyanates, or through the formation of allophanate and biuret. Cross-linking, whilst increasing hardness and abrasion resistance, improving the resistance to water, solvents, weathering and temperature can, if too high a level is used [2].

2.1.6 Definitions

In general, polyurethanes are produced by the reaction of a diisocyanate with a polyol illustrated below;

Scheme 2.1 Polyurethane reaction

This reaction is exothermic. The rate of polymerization reaction depends on the structures of both the isocyanate and the polyol. Aliphatic polyols with primary hydroxyl end-groups are the most reactive.

2.1.7 Reactions of Isocyanate

The isocyanate group (-NCO) can react with any compounds containing active hydrogen atoms, e.g. alcohol, carboxylic acid, amine, and water and diisocyanate may therefore be used to modify many other products.

Reaction with an alcohol yields urethane:

$RNCO + R'OH \longrightarrow RNHCOOR'$ (urethane)

Reaction with a carboxylic acid yields an amide:

$RNCO + R'COOH \longrightarrow RNHCOR'$ (amide) $+ CO_2$

Reaction with an amine yields a urea:

$RNCO + R'NH_2 \longrightarrow RNHCONHR'$ (urea)

Reaction with water produces a carbamic acid:

$RNCO + H_2O \longrightarrow RNHCOOH$ (carbamic acid)

$RNHCOOH \longrightarrow RNH_2$ (amine) $+ CO_2$

$RNCO + R'NH_2 \longrightarrow RNHCONHR'$ (urea)

Scheme 2.2 Reactions of isocyanate

The unstable carbamic acid breaks down into an amine and carbon dioxide. The amines react with a further molecule of isocyanate to form urea. This last reaction is one way of introducing gas to form foams but it is a reaction to be avoided in surface coatings.

Material selection

- Isocyanates

There are five isocyanates commonly used in coating formulations

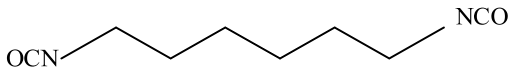
- MDI – 46 percent.
- Aliphatics – 37 percent (H_{12}MDI, HDI, IPDI).
- TDI – 17 percent.

Aliphatic isocyanates have a lower rate of reaction and from softer coatings than aromatic isocyanates when used in comparable formulations and are used where

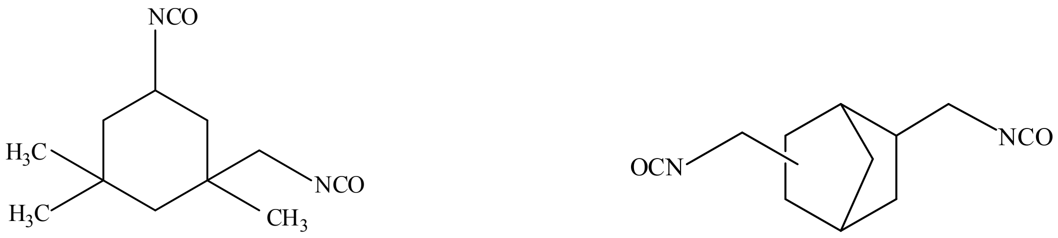
UV or light stability is required. For example in top-coats, and in water-borne systems. HDI and HDI adducts are the most widely used, with H_{12}MDI finding use in water-borne systems. For applications, which are not light sensitive, such as primers, and heavily pigmented maintenance coatings, then aromatic isocyanates are often preferred for economic reasons.

Aliphatic diisocyanates

Aliphatic diisocyanates are used in the manufacture of color-stable polyurethanes for coating and elastomer applications. Aliphatic diisocyanates afford polyurethane coating with outstanding weatherability.



Hexamethylene diisocyanate (HDI)



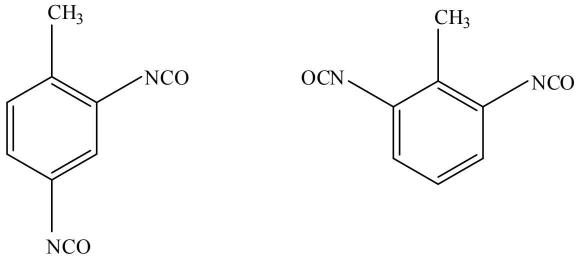
Isophorone diisocyanate (IPDI)

Norbornane diisocyanate (NBDI)

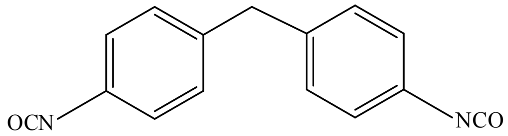
Figure 2.5 Types of aliphatic diisocyanate**.**

Aromatic diisocyanates

More than 90% of the total world production of isocyanates is accounted for polymeric MDI (PMDI), its co-product 4, 4'-methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).



2, 4 and 2, 6- toluene diisocyanate (TDI)



4, 4'-methylene diphenyl diisocyanate (MDI)

Figure 2.6 Types of aromatic diisocyanate.

Polyols

There are three main types of polyols used in coating technology with hydroxyl values in the range of 30 to 500 [2];

- Acrylics.
- Polyethers.
- Polyesters.

Acrylic polyol is amorphous, random copolymers prepared by the radical polymerisation of ester of acrylic and methacrylic acid plus vinyl monomers such as styrene with hydroxyl groups introduced through the use of hydroxylated methacrylates, such as hydroxyethyl methacrylate (HEMA). Three or more different monomers are normally used in the synthesis of acrylic polyols with the choice dependent on the manufacturing process, performance required and cost.

Acrylic and polyester polyols are generally preferred for harder coating with better weatherability. Care has to be taken in comparing the coating performance of systems based on the various types of polyol as it is strongly dependent on the level of branching and the hydroxyl value of the polyol. Nevertheless. Some general trends can be found that are applicable to all the isocyanates commonly used and these are shown in Table 2.2.

Table 2.2. Coatings performance versus polyol type

	Acrylic	**Polyester**	**Polyether**
Application conditions	Equal	Equal	Equal
Viscosity	Medium	High	Low
Appearance	Excellent	Very good	Good
Hardness	Hard	Medium	Soft
Brittleness	Fair	Excellent	Excellent
Gloss retention	Excellent	Fair	Poor
Solvnet resistance	Excellent	Fair	Fair
Salt water spray resistance	Excellent	Very good	Good

2.1.8 Aqueous polyurethane dispersion

The increase interest in waterborne coatings is due to its low VOC content. Waterborne coating technologies require new types of resins for binder dispersions and additives to fulfill high quality requirements. An aqueous PU dispersion (PUD) is a binary colloidal system in which the particles of PU are dispersed in continuous water phase. The particle size tends to be about 20-200 nm, and the particles have a high surface energy. This results in a strong driving force for film formation after water evaporation. Usually, PU polymers are not soluble in water and the degree of hydrophilicity is one of the key factors determining the particle size distributions in the PUD. The shelf life colloidal stability of PUD is influenced by their particle size distribution. Therefore, a special treatment or structural modification is necessary for the polymer to be dispersible in water. Generally, aqueous PUDs can be prepared by incorporating hydrophilic groups into the polymer backbone or by adding a surfactant. The former material known as a PU ionomer in which the ionic groups act as internal emulsifiers. Therefore, waterborne PU ionomers consist of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts.

Various process have been developed for the preparation of aqueous PUDs. In all of these processes, a medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates in the presence of an internal emulsifier as first step. The emulsifier is a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a non-ionic group [poly (ethylene oxide)] is usually added to allow the dispersion of the polymer in water. The critical step in which the various synthetic pathways differ is the dispersion of the prepolymer in water and the melecular weight buildup. The most important processes are the acetone process, pre-polymer mixing process, melts dispersion process and ketimine process.

Aqueous PUDs are of three types; non-ionic cationic and anionic depending upon the type of hydrophilic segments present in the PU backbone. Depending on the type of ionic species, a minimum ionic content is required for the formation of a stable PU ionomer. The interaction between ions and their counter ions is responsible for the formation of stable dispersion. The ion-dipole interaction between the ionomer and dispersing media (water) results in the formation of a salvation sheath, where the ionomer properties depends on the degree of neutralization and content of ionic component.

Amines

The amine compounds used in coating technology are polyoxyalkyleneamines, basically amine-tipped propylene oxide/ethylene oxide copolymers, and amine-terminated chain extenders, such as diethyl toluene diamine (DETDA) or isophorone diamine (IPDA) [2].

Solvents

Solvents have traditionally been added to reduce the viscosity of components, in order to improve processing; they should not react with isocyanates and need to have a water content of less than 500 ppm. These limitations do not apply to the non-reactive polyurethanes [2].

It is common practice to use a mixture of at least three solvents in order to dissolve every component in the system of form a stable emulsion. The solvents evaporate at different stages during film formation, some quickly, to avoid excessive sagging and dripping, whilst during the final stages slow evaporation is required to provide acceptable levelling and adhesion and to release stress in the coating. Solvents such as esters, ketones, ether-ester and polar aromatic and aliphatic solvents are split into the following three groups;

- Fast-boiling point under 100° C.
- Medium-boiling point 100 to 150°C.
- Tail or heavy-boiling point greater than 150°C.

There is a drive to reduce the solvent content of all formulations in every application due to the legislation that limits the levels of volatile organic compounds(VOCs) that can be emilled in some parts of the world. This is a major issue for aliphatic polyurethane spray coatings as these systems are generally based on high molecular weight polymers that need a high solvent level to obtain processable systems. This legislative pressure has led to the development of low viscosity polyol and isocyanate components leading to lower solvent usage (and also water-borne systems). Systems that contain more than 60wt-% or 70 vol-% non volatile are termed 'high solids' coatings. Because the amount of solvents required is strongly dependent on the application, the impact of recent legislation on VOCs is application specific.

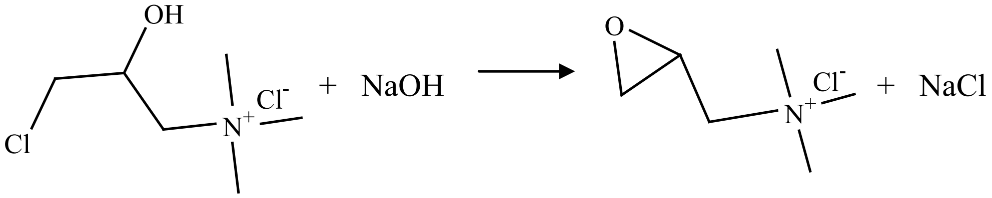
2.2 Literature Reviews

In 2007 Ho Tak Jeon [13] synthesized and characterized of waterborne polyurethane–silica hybrids using sol–gel process Using a sol–gel process nanometer-scale silicas were incorporated into waterborne polyurethanes (PUs) which were synthesized from Isophoronediisocyanate (IPDI), poly(tetramethyleneglycol) (PTMG), dimethylolpropionic acid (DMPA), triethylamine (TEA), diethylenetriamine (DETA) and 3-aminopropyltriethoxysilane as coupling agent. Thermal, mechanical and dynamic mechanical properties of the hybrid compositehave been studied. 29Si-NMR spectra gave evidence of condensation reaction between silica and silanes encaping the PU prepolymers, whereas transmission electron microscopy (TEM) showed the high connectivity of hybrid composites. It was found that greater thermal and mechanical properties of waterborne PU/silica hybrid composite were obtained when chemical networks were formed between PU and silica.

In 2006, Chien-Hsin Yang [14] studied of Hybrids of colloidal silica and waterborne polyurethane. Waterborne polyurethane (WPU) was synthesized and followed by adding colloidal silica to prepare WPU–silica hybrids. The silica content in the hybrid thin films was varied from 0 to 50 wt%. The experimental results revealed that the viscosity of these hybrid solutions increased with increasing silica content and resulted in the aggregation of silica particle in the hybrid films. The latter result was evidenced by SEM examination. The effect of interaction between silica particle and urethane polymer chains is more significant with increasing silica content. The prepared hybrid films show much better thermal stability and mechanical properties than pure WPU.

In 2009, Warayuth Sajomsang [4] prepared and characterized quaternary ammonium chitosan containing mono or disaccharide moieties. He synthesized by reductive *N*-alkylation then quaternized by *N*-(3-chloro-2-hydroxypropyl) Trimethyl ammonium chloride (Quat-188). The chemical structures of quaternary ammonium chitosan derivatives were characterized by ATR-FTIR and 1H NMR spectroscopy. The degree of *N*-substitution (DS) and the degree of Quaternization (DQ) were determined by ^{1}H NMR spectroscopic method. Moreover, all quaternary ammonium chitosan derivatives were highlywater-soluble at acidic, basic, and neutral pH. Minimum inhibitory concentration (MIC) antibacterial studies of these materials were carried out on *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria compared to quaternary ammonium*N*-octyl and*N*-benzyl chitosan derivatives. The quaternary ammoniummonoand disaccharide chitosan derivatives showedvery high MIC values whichwere in the range of 32 to >256_g/mL against both bacteria [4].

In 2005, Mohamed Hashem [15] studied crosslink of partially carboxymethylated cotton fabric via cationization. the cotton fabric was first partially carboxymethylated to impart to it the anionic character through its reaction with monochloroacetic acid in alkaline medium. Application of reactive cationic agent in alkaline medium affects crosslinking of the resulting anionic cotton in a second step. The reactive cationic agent used was 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188). Factors affecting the quaternization reaction of partially carboxymethylated cotton fabric (PCMC) have been studied. These factors include NaOH concentration, reaction time and temperature, quaternizing agent concentration as well as material to liquor ratio and method used for quaternization.



Scheme2.3. Reaction of 2.3-epoxidepropyl trimetyl ammonium chloride

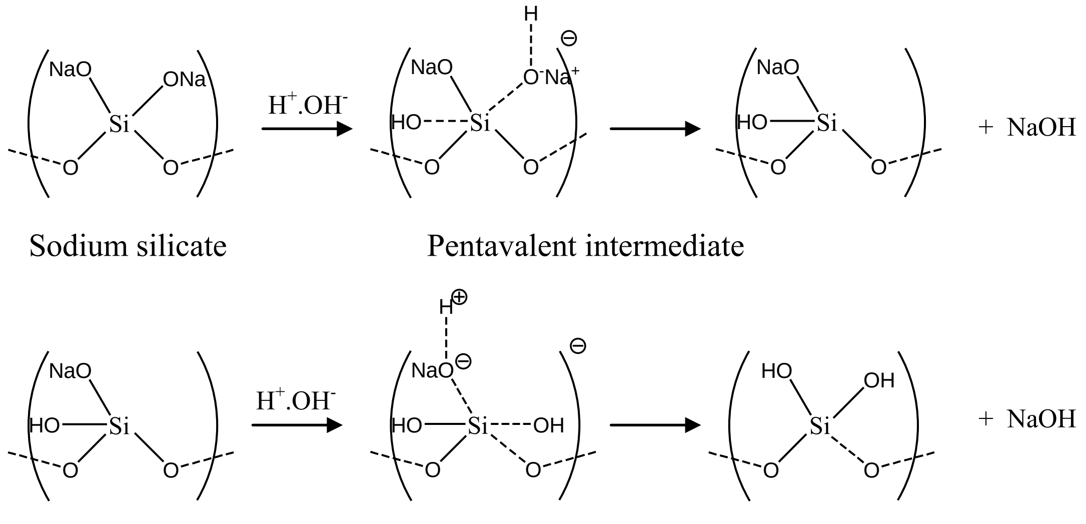
In 2006, Xia Xu [16] synthesized and antibacterial Activity of Nano-fumed Silica Derivative with N,N-dimethyl-n-hexadecylamine by used γ-Chloro propyl trimethoxysilane as the coupling agent. The nano-fumed silica derivative was characterized by FTIR. The zeta potentials of nano-fumed silica and nano-fumed silica derivative were measured as a function of pH in suspensions an showed the isoelectric point of modified nano-fumed silica has increased in the direction of pH rising compared with nano-fumed silica. Antibacterial properties of the nano-fumed silica derivative against selected microorganisms were tested by the quantitative suspension method. The result showed that the obtained polymer inhibited the growth of *E.Coli*, *S. Aureus* and *C. Albicans*. It was found that the growth inhibiting effect of polymer varied with the time exposed to microorganism. When the time exposed to the microorganism was 15 min, each of their inhibitory rates was 99.99%,99.99% and 95.23%, respectively.

In 2008 , Hila Elimelech [17] synthesized of polymer@silica submicrometer particles, which is based on the entrapment of a hydrophobic organic polymer in a polycondensating tetraethoxysilane (TEOS) oil-in-water (O/W) emulsion. As this system could not handle hydrophilic polymers, the development of a “mirror” W/O emulsion system was needed. Here we report the successful achievement of that goal, by demonstrating the synthesis of poly(ethyleneglycol)@silica submicrometer particles from (the cheaper, greener) sodium silicate, which is a less common monomer compared to TEOS in submicrometer silica particle synthesis. Indeed, finding the right conditions for preparing these particles required screening of many procedures, some of which are briefly mentioned. Full characterization of the hybrid particles is provided. As both PEG and silica are biocompatible, so are the hybrid particles.

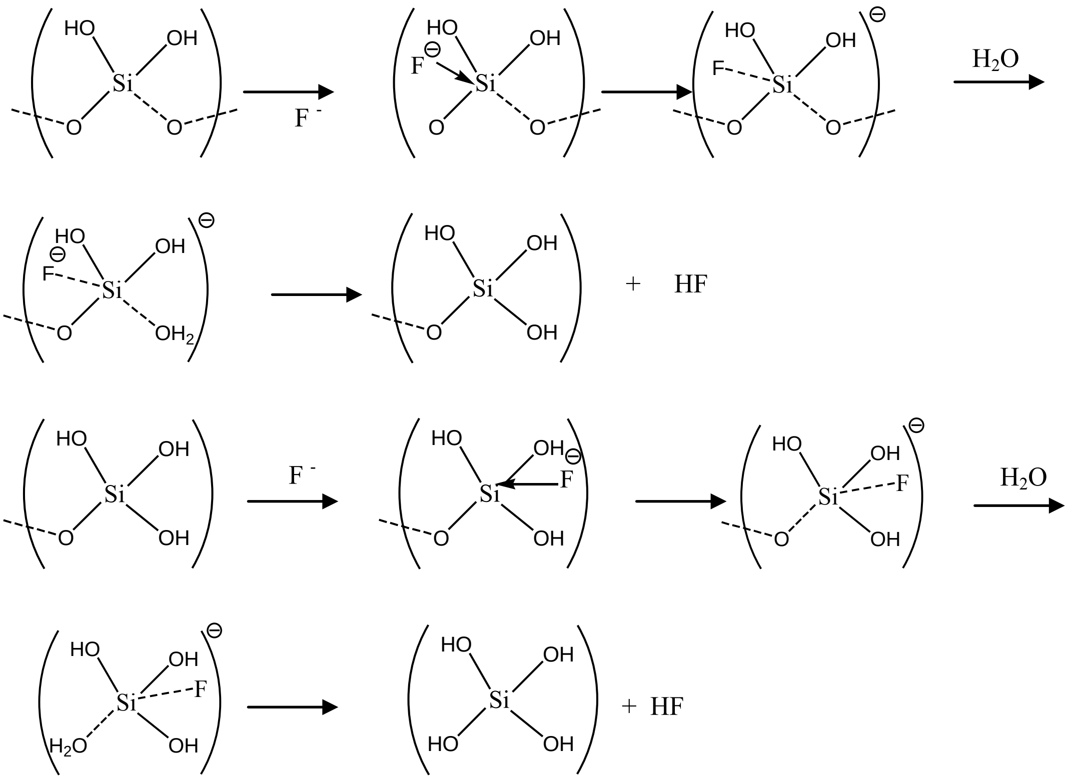
In 2008, Uzama K. [6] studied on physic-chemical properties of ambiently dried sodium silicate based aerogels catalyzed with various acids. He showed the reaction mechanism of acid clarifies at what extent he acid replaces the various groups from the precursor to form the silanols. From the following acid reaction mechanism, it is very clear that the branched structure of sodium silicate is transferred to the silicic acid. As an example, weak acid (CH_3COOH) has been considered.

Initially, the attack of H_2O on sodium silicate involves the displacement of two NaO^- groups via a bimolecular nucleophilic (SN2–Si) mechanism forming the NaOH as byproduct. In the next step, CH_3COO^- attacks the Si atom from back side resulting in a pentavalent intermediate, which on further nucleophilic attack of H_2O displaces the first O atom of O–Si–O chain producing CH_3COOH as byproduct. In the third step, again CH_3COO^- attacks the Si atom from front side which follows the second step to replace the second O atom of the O–Si–O chain giving the final product as silicic acid.

Acid reaction mechanism



Scheme 2.4 Synthesis of silic acid

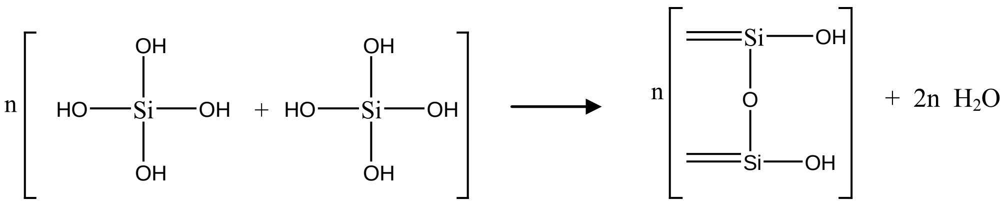


Hydrolysis

$Na_2SiO_3 + H_2O \xrightarrow{Acid} Si\,(OH)_4$ + Sodium salt

Sodium silicate Silicic acid

Condensation



Scheme 2.4 (cont.). Synthesis of silic acid

In 2008, I.A. Rahman [18] Synthesis of organo-functionalized nanosilica via a co-condensation modification using 3-aminopropyltriethoxysilane (APTES). An easy and swift pathway in preparation of organo-functionalized silica in nanosize range with amine-terminated group via co-condensation method is reported. The process is a self-catalyzed reaction by amine group of organosilane without the addition of ammonia as a catalyst at room temperature. A modified nanosilica with particle size of _60 nm, highly monodispersed and low aggregation was successfully produced.

In 2002, Teofil Jesionowski [19] prepared of the hydrophilic/hydrophobic silica particles. Studies on the surface modification of silicas using silane coupling agents are described. Chemical modification of silica surface using alkoxysilanes has been reported by many researchers. Low concentration of APTES solutions was often used to modify silica surfaces. This report showed that low concentration of silane coupling agents has prevented the occurrence of multi-layer adsorption of alkoxysilanes on the silica surface.

In 2009, Pradip B [20] produced of low-density sodium silicate-based hydrophobic silica aerogel beads by a novel fast gelation process and ambient pressure drying process. The beads were prepared by acid-base sol-gel polymerization of sodium silicate in aqueous ammonia solution via the ball dropping method (BDM). To minimize shrinkage during drying, wet silica beads were initially prepared; their surfaces were then modified using trimethylchlorosilane (TMCS) via simultaneous solvent exchange and surface modification. The effect of the volume percentage (%V) of TMSC on the physical and textural properties of the beads increased with an increase in the %V of TMCS.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Chemicals	Suppliers
Isophorone diisocyanate (IPDI)	ACROS
N-methyl-2-pyrrolidone (NMP)	ACROS
Dimethylolpropionic acid (DMPA)	ACROS
Triethylamine (TEA)	FLUKA
Diethylenetriamine (DETA)	FLUKA
Sodium Silicate	Siri Silicate
3-chloro-2-hydroxypropyl trimethylammonium chloride (Quat-188)	DOW Chemical
Sodium Hydroxide	ACROS
3-amino propyl triethoxysilane APTES	Degussa
Poly(tetramethylene ether)glycol PTMG (1000 Mw)	Siam Chemical Industry
Silica fume Aerosil 200	Degussa
Toluene	FLUKA
Ethanol	FLUKA
Acetic Acid	FLUKA

3.2 Glasswares and Equipments

1. Burette
2. Pipette
3. Ultra turrax disperser (UTD)
4. Mechanical stirrer
5. Thermometer

6. Condenser
7. Five-neck round bottom glass reactor
8. Heating mantle
9. Silicone oil bath
10. Dropping funnel
11. Round bottom glass reactor
12. High speed centifuge
13. Oven
14. High speed dispenser

3.3 Instruments

1. Fourier Transform infrared spectrometer, FTIR
2. Solid State NMR
3. Thermogravimetric Analysis (TGA)
4. Differential scanning calorimeter (DSC)
5. Transmission electron microscope, TEM
6. Instrument for Antibacterial activity Testing
7. Bar applicator 100 micron
8. Pencil hardness tester (6B, …, HB, F, H,…, 6H)

3.4 Purification and Preparation of Materials

3.4.1 Water was removed from polyester polyol by heating in vacuum oven at 120ºC for 2 h.

3.4.2 Water was removed from dimethylolpropionic acid (DMPA) by heating in vacuum oven at 105ºC for 2 h.

3.4.3 *N*-methyl-pyrolidone (NMP) was purified before used by refluxing with calcium hydride (CaH_2) for 2 h and then distilling off.

3.4.4 Water was removed from triethylenediamine by immersing molecular sieve type 4A for 24 h and then distilling off.

3.5 Synthesis of waterborne polyurethane containing quaternized silica

3.5.1 Synthesis of silica

Silica was prepared by hydrolysis and polycondensation of sodium silicate solution in the presence of acetic acid was shown in Figure 2.1. Silica was prepared by adding 3.0 N acetic acid [20] solution dropwise to sodium silicate solution followed by stirring. For gelation, temperature was kept at 50 °C in a temperature-controlled oven to form a gel. After gelation, the gel was aged for 3 h at 50 °C to strengthen the gel network. The gel was then washed with distilled water 3 times in 24 h [21]. To remove the sodium ions partially from the gel network. Next, methanol was exchanged with the gel, then the sample was separated from the solution by centrifugation at 8000 rpm and washed thoroughly one time with methanol. Next dry washed alcogel obtained by ambient drying were heated at 110ºC. The resulting sample was denoted silica.

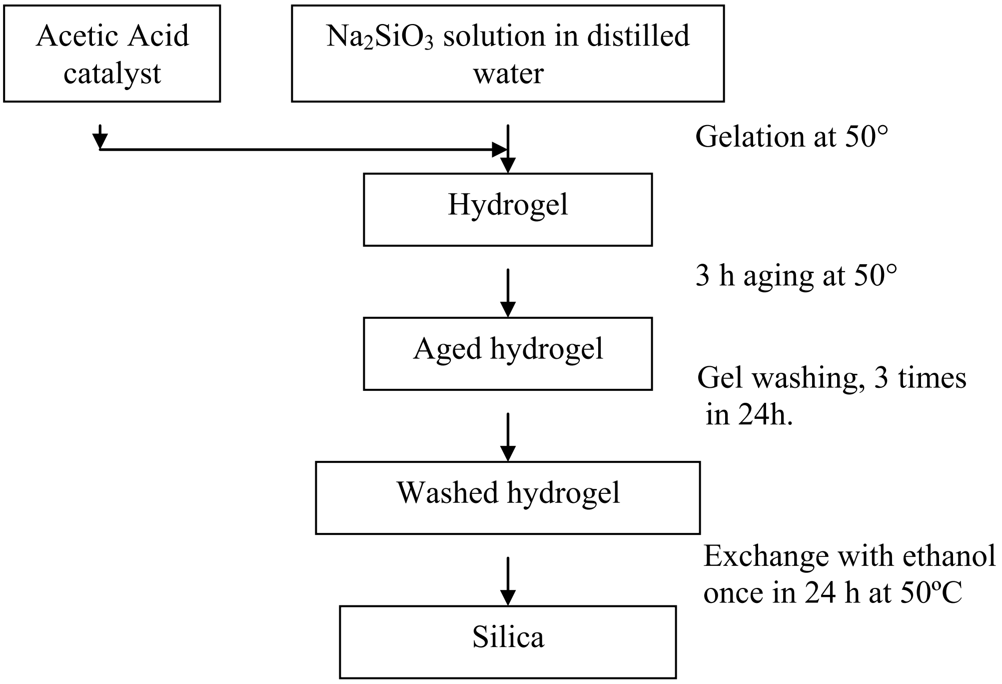
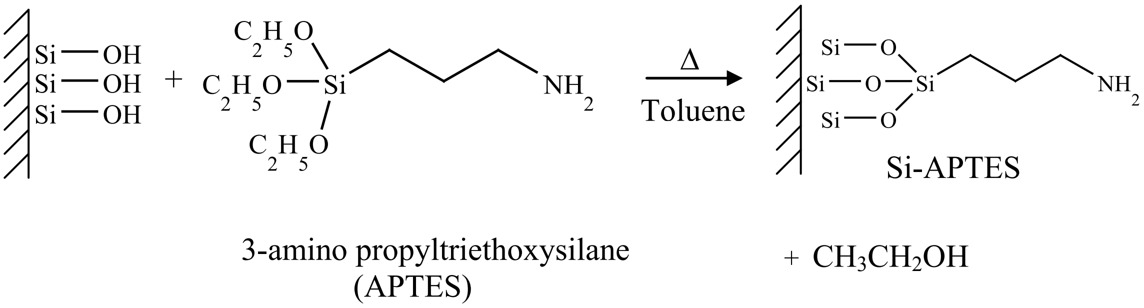


Figure 3.1 Preparation scheme for the synthesis of silica

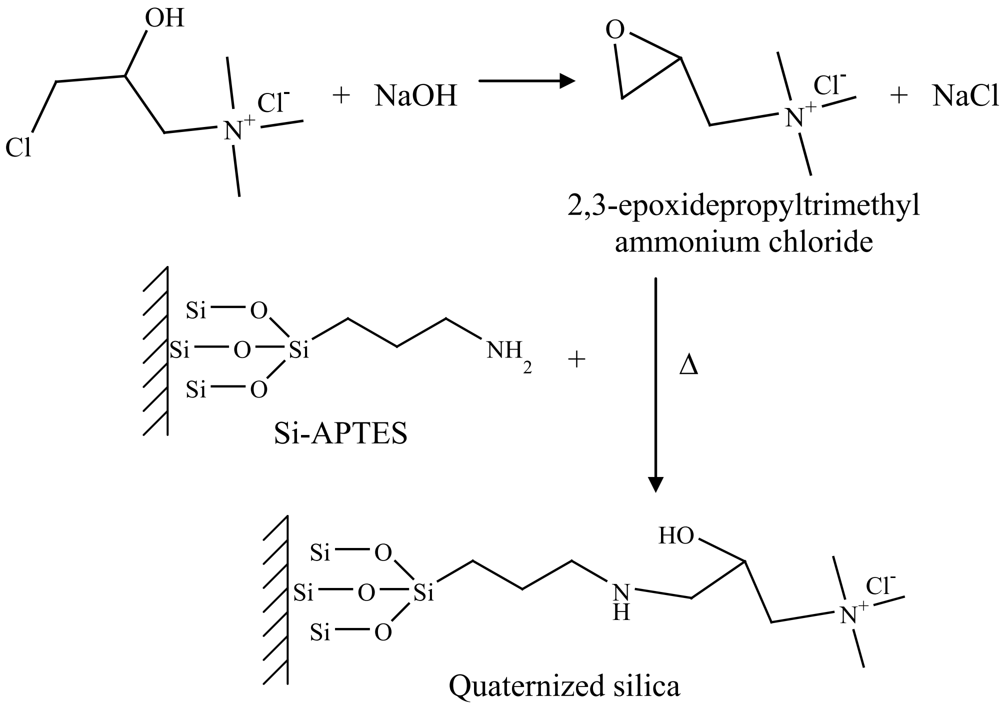
3.5.2 Synthesis of the surface modification silica with silane coupling agent



Scheme 3.1. Synthesis of Si-APTES from sodium silicate.

A sample of 2 g of silica was mixed with 65 ml of APTES solution (1% v/v in toluene). The mixture was agitated for 24 h under reflux at 110ºC. The sample was then separated from the solution by centrifugation at 8000 rpm and washed thoroughly three times with toluene. Washed samples as were cured at 110ºC for 12 h in a conventional oven. The resulting sample was denoted as Si-APTES [22].

3.5.3 Synthesis of quaternized silica



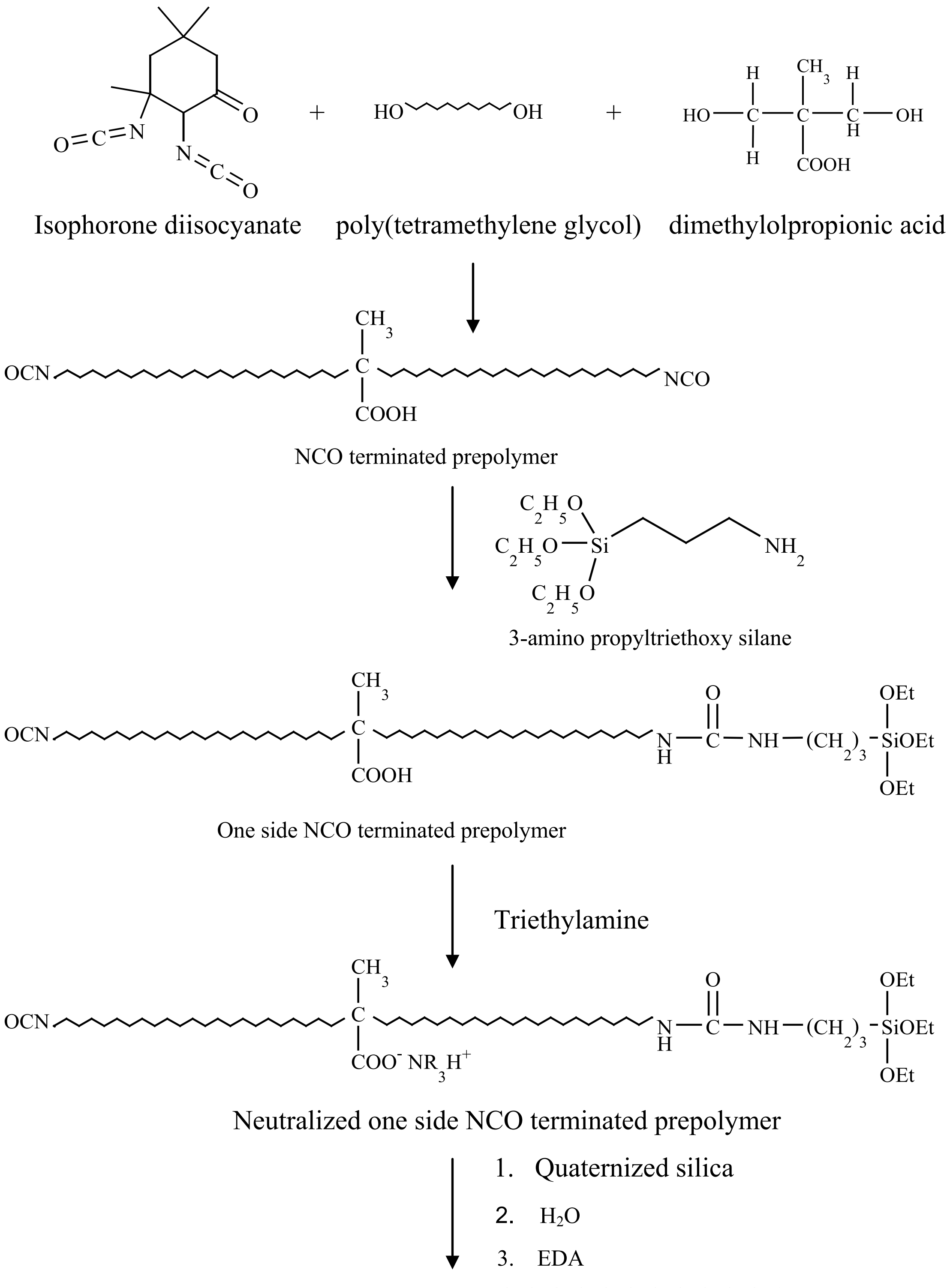
Scheme 3.2. Synthesis of quaternized silica.

A sample of 2 g of Si-APTES was mixed with 3-chloro-2-hydroxypropyl trimethylammonium chloride (Quat-188) was raised to pH 8 by using 15% (w/v) sodium hydroxide for 24 h using a magnetic stirrer. The weight ratio between Si-APTES and Quat-188 was varied, by changing the amount of Quat-188 introduced while keeping the amount of Si-APTES constant as described Table 3.1. Yellowish white solid was then separated from the liquid phase by centrifugation at 8000 rpm and washed thoroughly with DI-water several times until the washed water was negative to silver nitrate solution. This indicated that no free Quat-188 was on the yellowish white solid. The sample was dried at 100°C to remove water and was denoted quaternized silica [4].

Table 3.1 Recipe for the preparation of quaternized silica particles.

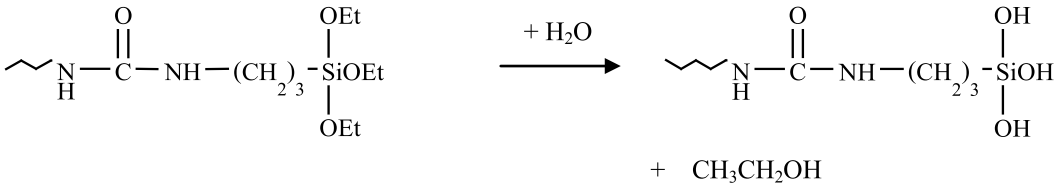
Sample	Si-APTES	Quat-188 reacted with 15% w/v of NaOH
(No.)	(g)	(ml)
1	2	25
2	2	35
3	2	45
4	2	55
5	2	65
6	2	-

3.5.4 Synthesis of Aqueous Polyurethane Dispersion

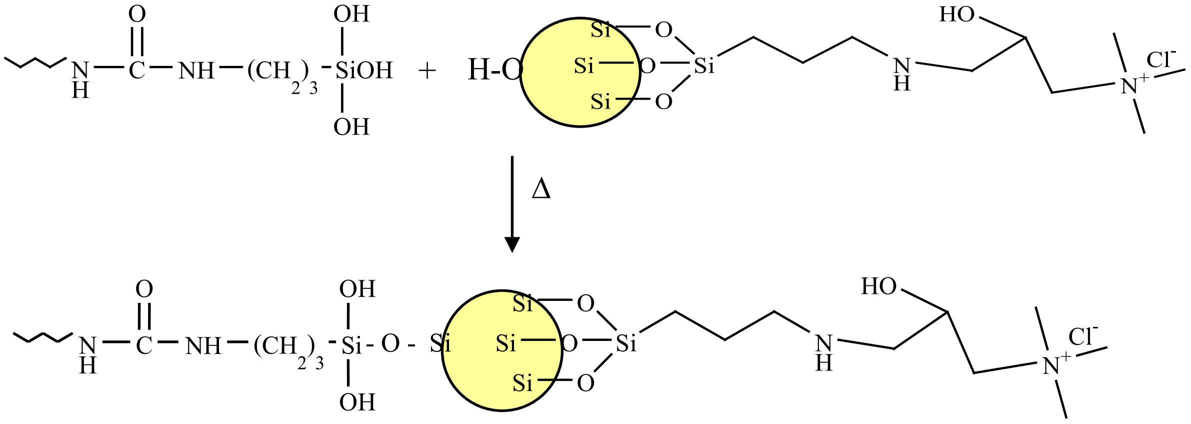


Scheme 3.3. Reaction scheme to prepare waterborne polyurethane containing quaternized silica

Hydrolysis



Condensation



Scheme 3.4. The scheme for the sol-gel process of waterborne polyurethane containing quaternized silica.

A 500 ml round bottom, five-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube was used as reactor. The reaction was carried out in a constant temperature oil bath. The overall reaction scheme is shown in Scheme 3.3. PTMG, IPDI, and DMPA (4 %wt based on polyurethanes) were mixed and reacted in the presence of DBTDL (0.03 phr based on the total solid) for 2 h at 80ºC to obtain NCO-terminated prepolymer. Subsequently to cap one terminal of NCO group of prepolymer, 3-aminopropyltriethoxysilane as a coupling agent was added and reacted for another 2 h at 50ºC. After cooling the reaction mixture to room temperature, TEA and quaternized silica were fed into the reactor and mixed thoroughly for 3 h to neutralize DMPA unit and to disperse quaternized silica in polyurethanes. Quaternized silica was varied at different weight ratio as showed in Table 3.2. An aqueous dispersion of NCO-terminated prepolymer was obtained by adding water (30ºC) to the mixture. Since the water addition rate is a critical parameter to obtain a stable emulsion, water was fed for 20 min at a constant flow rate. The sol–gel process is occurred at this step. APTES can undergo a variety of reactions during the preparation of a hybrid by a sol–gel route. Hydrolysis of ethoxy groups in PU gives silanol groups which can subsequently condense with silanol groups on the quaternized silica to form siloxane. The Si atom in APTES is tri-functional in terms of reactive ethoxy groups and is therefore able to form a three-dimensional chemical bondings between PU and quaternized silica [13]. The scheme for the sol–gel process of PU and quaternized silica is summarized in Scheme 3.4. EDA dissolved in water (3 %wt) was then fed to the emulsion at 50 ºC and chain extension with EDA was carried out for 1 h. The resulting product was a PU emulsion with a solid content of about 30%. The recipes to prepare of waterborne polyurethane containing quaternized silica composites are shown in Table 3.2.

Table 3.2. Recipe for the preparation of waterborne polyurethane containing quaternized silica composites.

Designation	Sample (g)										
Substance	PU1	PU2	PU3	PU4	PU5	PU6	PU7	PU8	PU9	PU10	PU11
PTMG (1000 g/mol)	59.5	59.5	59.5	59.5	59.5	59.5	59.5	59.5	59.5	59.5	59.5
IPDI	26.1	26.1	26.1	26.1	26.1	28.7	31.3	31.3	31.3	31.3	31.3
Aminosilane	6.5	-	-	-	6.5	6.5	6.5	6.5	6.5	6.5	6.5
DMPA	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9
DETA	1	1	0.5	-	-	-	-	-	-	-	-
EDA	-	-	-	1	1	1	1	1	1	1	1
TEA	3	3	3	3	3	3	3	3	3	3	3
Aerosil 200	2	-	-	-	2	2	2	-	-	-	-
Quaternized silica	-	-	-	-	-	-	-	2	3	4	5

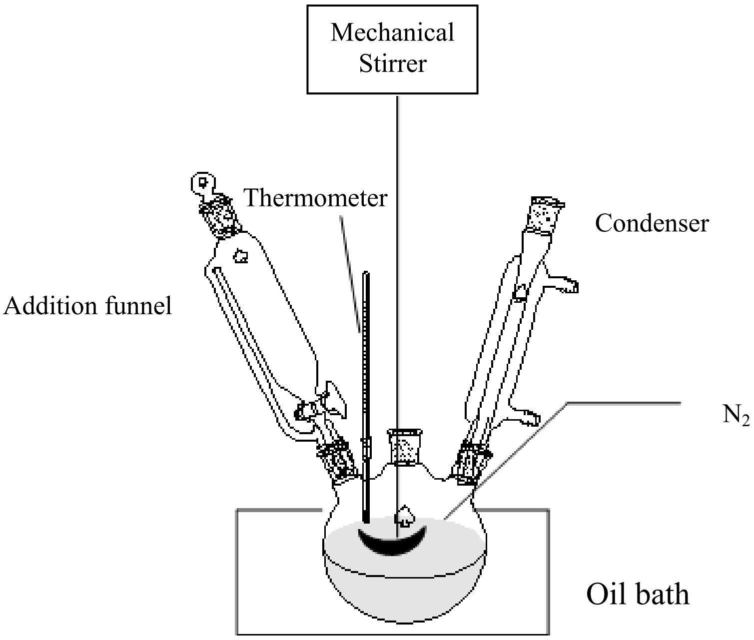
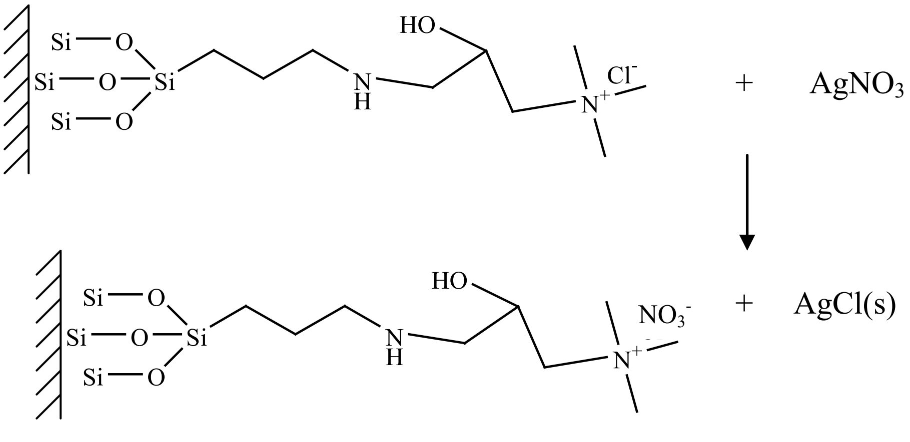


Figure 3.2 The apparatus for the synthesis of waterborne polyurethane containing quaternized silica.

3.6 Determination of Properties of sample

There are two items of specification determined here namely; Amount of incorporate Quat-188 and silanol concentration of silica modified, One item of specification determined of polyurethane is nonvolatile matter (NV). Each of them will be described as follows.

3.6.1 Determination of the amount of incorporated Quat-188



Scheme 3.5. Determination of the amount of incorporated Quat-188

The amount of Quat-188 incorporated on quaternized silica was determined by titrating with 0.017 M silver nitrate in DI water. The indicator solution was made by dissolving potassium chromate (0.250 g, 1.287 mmol in deionized water 20 mL). Quaternized silica (~0.2xxx g) was dissolved in deionized water (25 mL) and then 0.064 mM potassium chromate was added (0.5 mL). After stirring for 10 minute, the solution was titrated with 0.017 M silver nitrate, until the end-point of the reaction was reached, as evidence by the formulation of the red-brown precipitate silver chromate.

3.6.2 Determination of silanol concentration

The concentration of silanol groups were determined through alkali neutralization method described in literature [23]. Wg of a sample was mixed with 50 ml of 0.05M aqueous solution of NaOH in a 100 mL conical flask. The flask was sealed and then stirred for 12 h. The mixture was centrifuged and 10 ml of supernatant was collected and then titrated against standardized 0.05M aqueous solution of HCl (A mL) using 0.1% phenolphthalein as indicator. The above procedures were repeated with blank solution. The amount of HCl consumed for neutralization was designated as B ml. The amount of total hydroxyl group (X mmol g^{-1}) per unit grams of the silica was estimated according to the following formula:

$$X = \frac{(B - A) \times 0.05 \times 5}{W}$$

3.6.3 Determination of Nonvolatile Matter (NV): ASTM D 2834-95

Place approximately 2 g of aqueous polyurethane dispersion into a flat-bottom dish and place in the oven maintained at 105.0 ± 2.5°C. After heating for 24 h, weigh the dish [24].

$$\%NV = \frac{[(C - A)] \times 100}{S}$$

C = weight of dish and contents after heating (g)
A = weight of dish (g)
S = weight of sample used (g)

3.7 Characterization

All product of silica, Si-APTES, quaternized silica, waterborne polyurethane and waterborne polyurethane containing quaternized silica were characterized by FTIR, solid state ^{13}C NMR and ^{29}Si NMR spectroscopy.

3.7.1 FTIR Analysis

Fourier transform infrared (FTIR) spectra of silica, silica modified surface, Waterborne polyurethane, Waterborne polyurethane containing quaternized silica were obtained using a Bruker Tensor 27 FTIR spectrometer in the range 400–4000 cm^{-1} at room temperature, employing the KBr disc technique.

3.7.2 Solid State NMR

All samples were characterized at room temperature (20+/- ºC) with solid state ^{13}C, ^{29}Si NMR. The spectra of ^{13}C, ^{29}Si NMR were recorded on a AVANCE 300 MHz Digital NMR Spectrometer Bruker Biospin DPX-300 at a frequency of 75 and 60 MHz, respectively.

3.8 Antibacterial activity

In order to assess antibacterial function of quaternized silica, the suspension quantitative test was employed. The bacteria used were *E.coli* (8099), *S.aureus* (ATCC6538). Quaternized silica 20 mg was added to a tube containing 1 ml of 10^7 cfu of *E.coli* and 9 ml normal saline solution. The resulted solution was thoroughly mixed at 37°C by using a Burrell wrist action shaker for 24 h., and left it stand for 30 min. 10 µl Supernatant of the mixture was diluted 50% gradiently. It was then added to agar plate and incubated at 37°C for 24 h. After incubation, the colonies of bacteria were counted to indicate antibacterial activity.

In this work, the degree of antibacterial or bacteriostatic effect was presented as the reduction ratio of the bacteria. The equation for quantitative antibacterial evaluation is given by:

$$R(\%) = \frac{A - B}{A} \times 100\%$$

Where R is the percentage reduction ratio, A the number of bacterial colonies from the untreated bacteria suspension (without Quat-188 supported silica powders) and B is the number of bacterial colonies from the bacteria suspension treated by quaternized silica for 24 h [16,25].

3.9 Mechanical properties

3.9.1 Morphology of particles

The morphology of particles in waterborne polyurethane-silica hybrid and waterborne polyurethane containing quaternized silica were observed by transmission electron microscopy (TEM) JEM-200CX model. Samples for TEM observation were prepared by dropping highly diluted latex onto the formvar-coated copper grid, stained with phosphotungstic acid or osmium tetraoxide, and dried in a desiccator at room temperature.

3.9.2 Differential scanning calorimetry (DSC)

DSC measurements were performed to determine the reactivity of silica and epoxide groups (Quat-188) grafted onto silica using a Perkin-Elmer DSC-7 instrument. Aluminium pans containing 12–15 mg of sample were heated from 0ºC to 250ºC. The heating rate was 10ºC/min.

3.9.3 Thermogravimatric analysis (TGA)

TGA was carried out to determine the thermal stability of the modified silica samples under nitrogen using a Mettler ToledoTGA/SDTA 851e instrument. Samples (~10 mg) was placed in an alumina pan and heated to 600ºC (10ºCmin^{-1}).

3.9.4 Pencil hardness

Waterborne polyurethane and polyurethane containing quaternized silica were tested Pencil hardness test (ASTM D-3363)[26].

1. Apply the surface coating by appropriate means to a smooth rigid glass and cure 7 days.
2. The film thickness of the coating shall be wet film 100 micron.
3. Conduct the test at 23±2°C and 50±5 % relative humidity.
4. Place the coated panel on a level, firm, horizontal surface. Starting with the hardest lead, hold the pencil or lead holder firmly with the lead against the film at a 45° angle (point away from the operator) and push away from the operator. Exert sufficient uniform pressure downward and forward either to cut or scratch the film or to crumble the edge of the lead. It is suggested that the length of the stroke be 6.5 mm (1⁄4 in.).
5. Continue the process until a pencil is found that will neither cut through nor scratch the surface of the film. Record end point for scratch hardness.

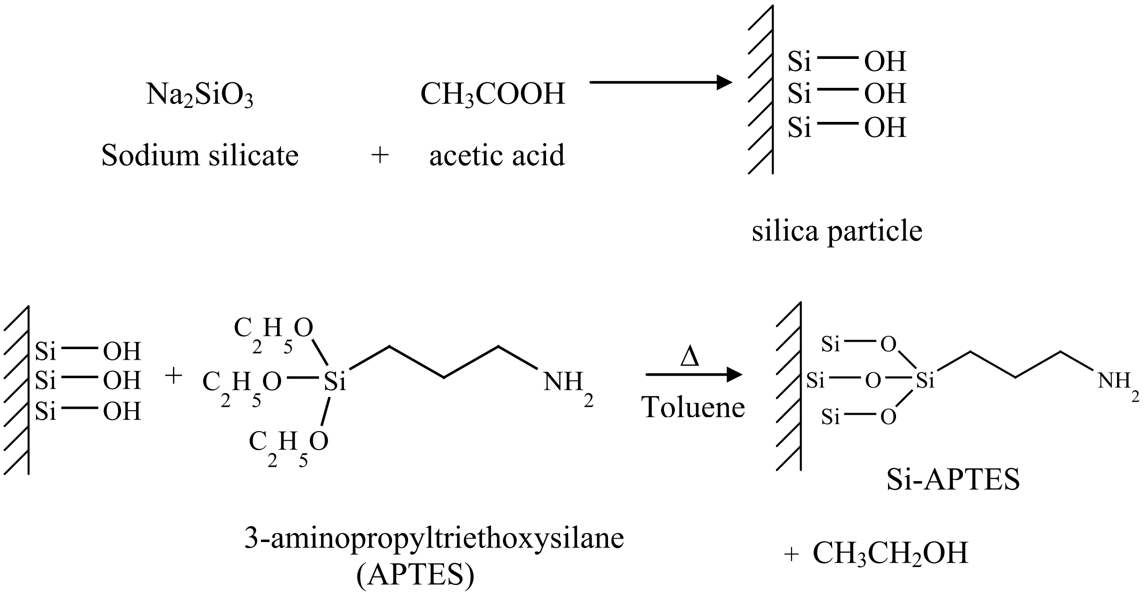
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of quaternized silica

4.1.1 Preparation of Si-APTES

In this research, silica particle was synthesized from sodium silicate solution by reacting with acetic acid as described in section 3.5.1. It was observed that during the addition of acetic acid into sodium silicate solution, the mixture became more viscous indicating the gel formation. After the reaction was complete, silica was separated by centrifugation. The surface of silica particle was then modified with 1% v/v of 3-aminopropyltriethoxysilane (APTES) in toluene according to the method reported by P. Vejayakumaran et al [22]. Scheme 4.1 showed the preparation of Si-APTES from sodium silicate. The resulting sample was denoted Si-APTES.



Scheme 4.1. Preparation of Si-APTES from sodium silicate

4.1.1.1 FTIR analysis

Synthesis of silica was confirmed from functionality of silanol by analyzing it with FTIR spectroscopy. Figure 4.1 shows the absorption band at around wave number 3400 cm^{-1} which confirms free hydroxyl functional group in the synthesized silica. The presence of the absorption sharp and strong Si–O–Si stretching signal at~1100 cm^{-1} was observed for all surface modified samples, indicating that the main structure was not changed by the modification reactions. The signal observed at ~ 1638 cm^{-1}indicates the presence of physically adsorbed water in the silica sample [19-23].

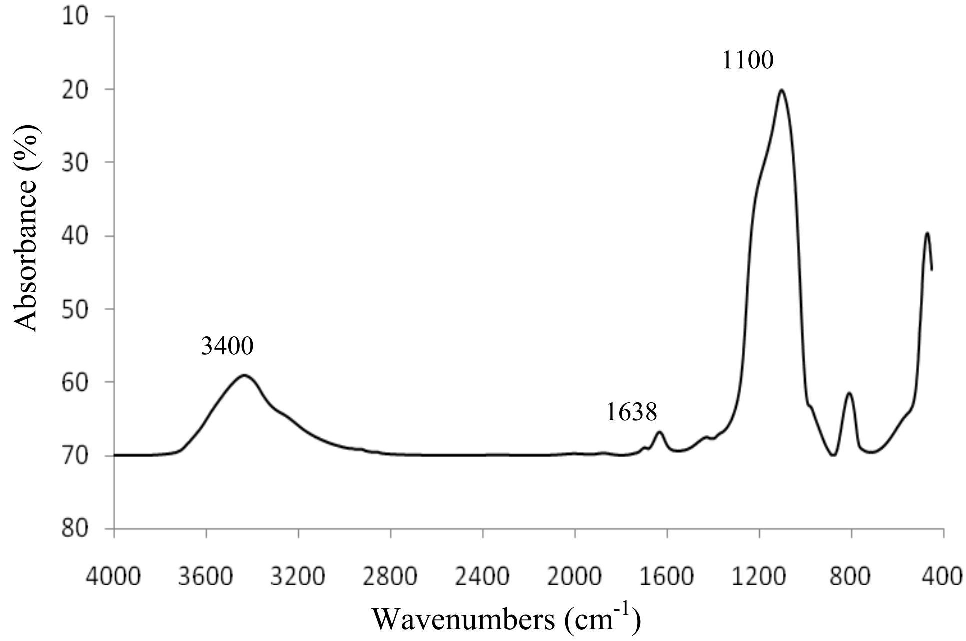


Figure 4.1. FTIR spectrum of pure silica.

Figure 4.2 shows FTIR spectrum of synthesized Si-APTES from sodium silicate solution. The FTIR spectrum of Si-APTES showed absorption at 2920 cm^{-1} is due to C-H stretching, which indicates the presence of $–CH_2$ groups. The shoulder observed at ~1560 cm^{-1} (N-H bending) indicates the presence of $–NH_2$ groups. The signal corresponding to N-H stretching is expected to overlap with the stretching vibrations of O-H groups at ~3500 cm^{-1}[19-23].

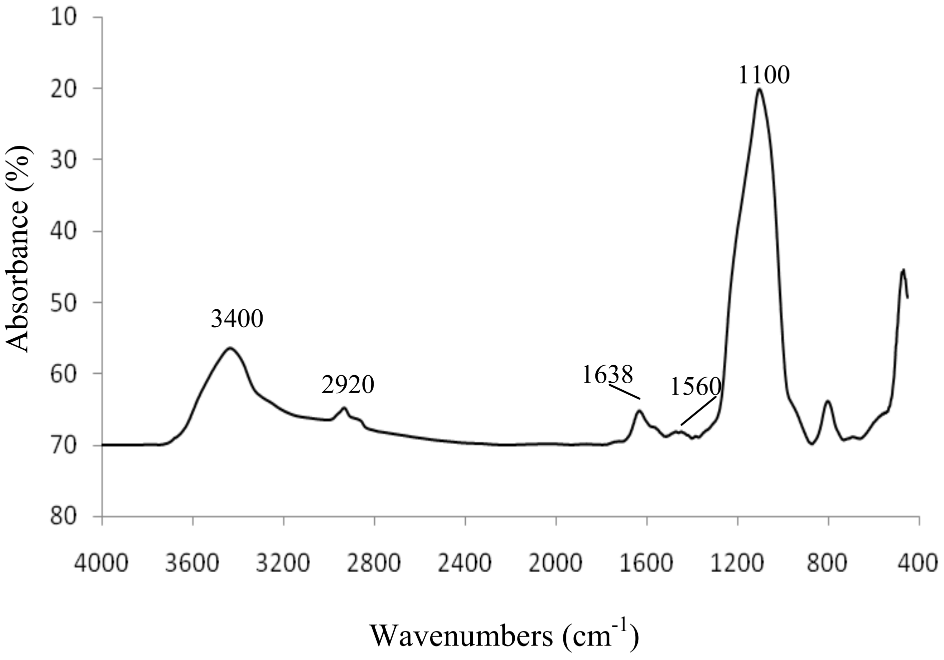


Figure 4.2. FTIR spectrum of Si-APTES.

4.1.1.2 Solid state NMR analysis

^{29}Si NMR measurements were performed to determine the surface structure of silica particles modified with various organo functional groups. Figure 4.3 shows the ^{29}Si NMR spectrum of pure silica particles. The pure silica particles showed signals representing Q_4 ($Si(OSi)_4$, siloxane), Q_3 ($Si(OSi)_3OH$, silanol), Q_2 ($Si(OSi)_2OH_2$) species at −110.51 ppm, −100.50 ppm and 92.14 ppm, respectively. Pure silica was no signals observed in ^{13}C NMR spectrum [27].

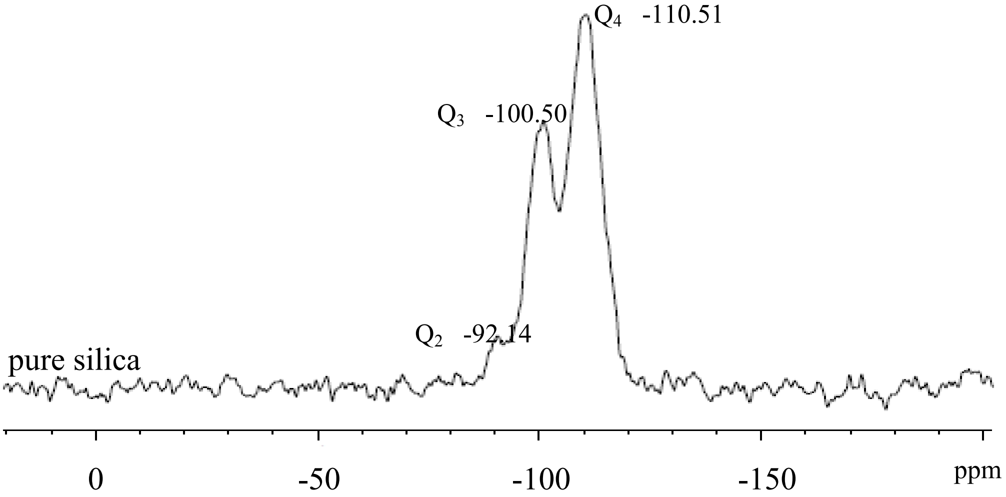


Figure 4.3. ^{29}Si NMR spectrum of pure silica

Figure 4.4 shows the ^{29}Si NMR spectrum of Si-APTES. Si-APTES showed signals representing Q_4 ($Si(OSi)_4$, siloxane) and Q_3 ($Si(OSi)_3OH$, silanol) species at −110.21 ppm and −100.71 ppm, respectively. Besides these two signals, additional signals were observed for all the surface modified silica particles. Si-APTES showed one broad signal at −65.79 and -57.89 ppm, corresponding to T_3 ($RSi(OSi)_3$)and T_2 ($RSi_2(OSi)_2$) species, in which R represents the aminopropyl group in the APTES molecule [27].

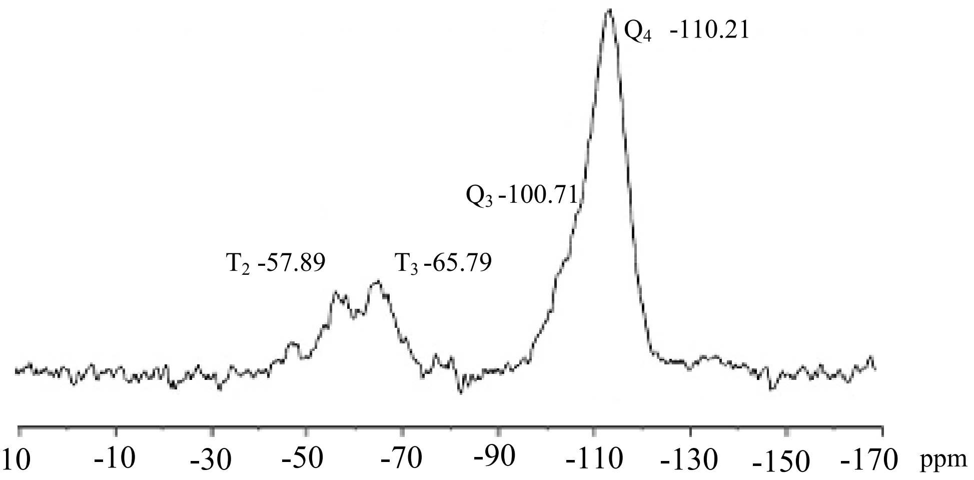


Figure 4.4. ^{29}Si NMR spectrum of Si-APTES

The ^{13}C NMR spectrum of Si-APTES shows three prominent signals at 8.6 ppm (C1), 20.9 ppm (C2) and 42.1 ppm (C3). The proposed structure was shows with corresponding signal assignments in Figure 4.5.

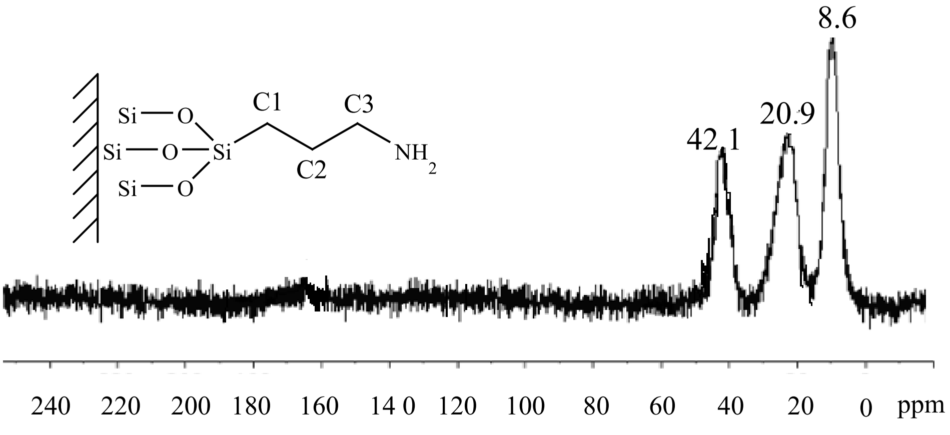
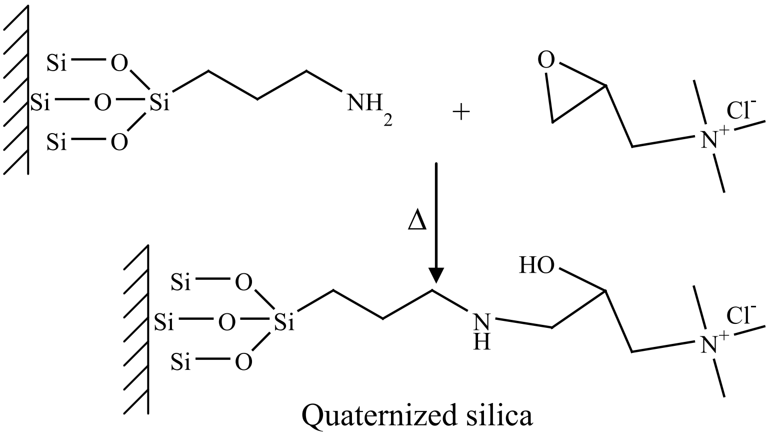


Figure 4.5. ^{13}C NMR spectrum of Si-APTES

4.1.2 Quaternization of Si-APTES

Quaternization of Si-APTES was synthesized with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188) as shown in Scheme 4.2, The weight ratio between Si-APTES and Quat-188 was varied, by changing the amount of Quat-188 introduced while keeping the amount of Si-APTES constant as described in section 3.5.3. The yellowish white solid was then separated from the liquid phase by centrifugation. It was then washed with water several times until the washed water was negative to silver nitrate solution. This indicated that no free Quat-188 was on the yellowish white solid.



Scheme 4.2. Synthesis of quaternized silica

4.1.2.1 FTIR analysis

Figure 4.6 showed spectra of (a) pure silica, (b) Si-APTES and (c) quaternized silica. The FTIR spectra observed absorption signal Si-O-Si at 1100 $cm^{-1}$and O-H at 3400 cm^{-1} and 1638 cm^{-1} for all surface modified samples, indicating that the main structure was not changed by the modification reaction. The spectrum of quaternized silica showed absorption at 2920 cm^{-1}(C-H stretching), which indicated the presence of $-CH_2$ groups. Additional signal was observed for quaternized silica compared to the Si-APTES at 1477 cm^{-1} corresponding to $N^+(CH_3)_3$ stretching [4,9].

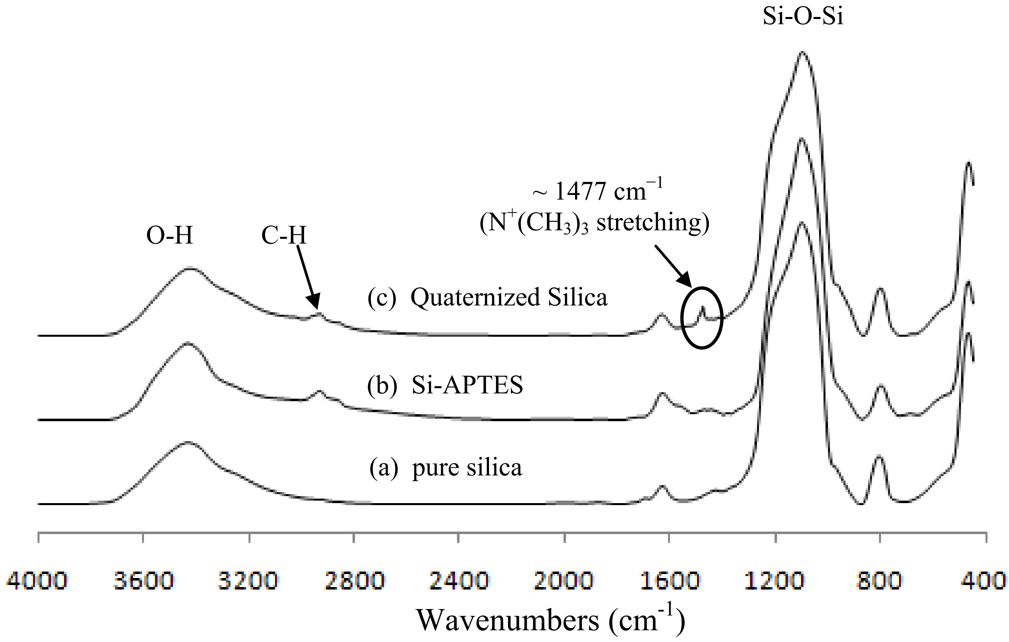


Figure 4.6. FTIR spectra of pure silica, Si-APTES and quaternized silica

4.1.2.2 Solid State NMR analysis

Synthesis of quaternized silica was confirmed from functionality of Quat-188 by analyzing it with solid state NMR spectroscopy. Figure 4.7 showed the ^{29}Si NMR spectra of pure silica, Si-APTES and quaternized silica. Quaternized silica particles (Figure 4.7(c)) showed signals representing Q_4 ($Si(OSi)_4$, siloxane), Q_3 ($Si(OSi)_3OH$, silanol), Q_2 ($Si(OSi)_2OH_2$) and T_3 ($RSi(OSi)_3$, crosslinked) species at −110.13 ppm, −100.77 ppm, 91.60 ppm, -65.87 ppm and -57.27 ppm respectively. Interestingly, quaternized silica in Figure 4.7(c) exhibited a similar ^{29}Si NMR spectrum to Si-APTES. This indicates that the Quat-188 molecules did not react with the silica surface [22]. APTES modification caused the decrease of the Q_3 silanols signal intensity, that exhibited comparision between Figure 4.7 (a) and Figure 4.7 (b). The emergence of signal in the typical chemical shift region of T_2 and T_3 atoms. This confirms the occurrence of condensation, in agreement with ^{13}C NMR data. From Figure 4.7 (b) and Figure 4.7 (c), Figure 4.7 (c) was showed the higher of the Q_3 silanols signal intenisity, because water in Quat-188 hydrolyzed with silica surface [28].

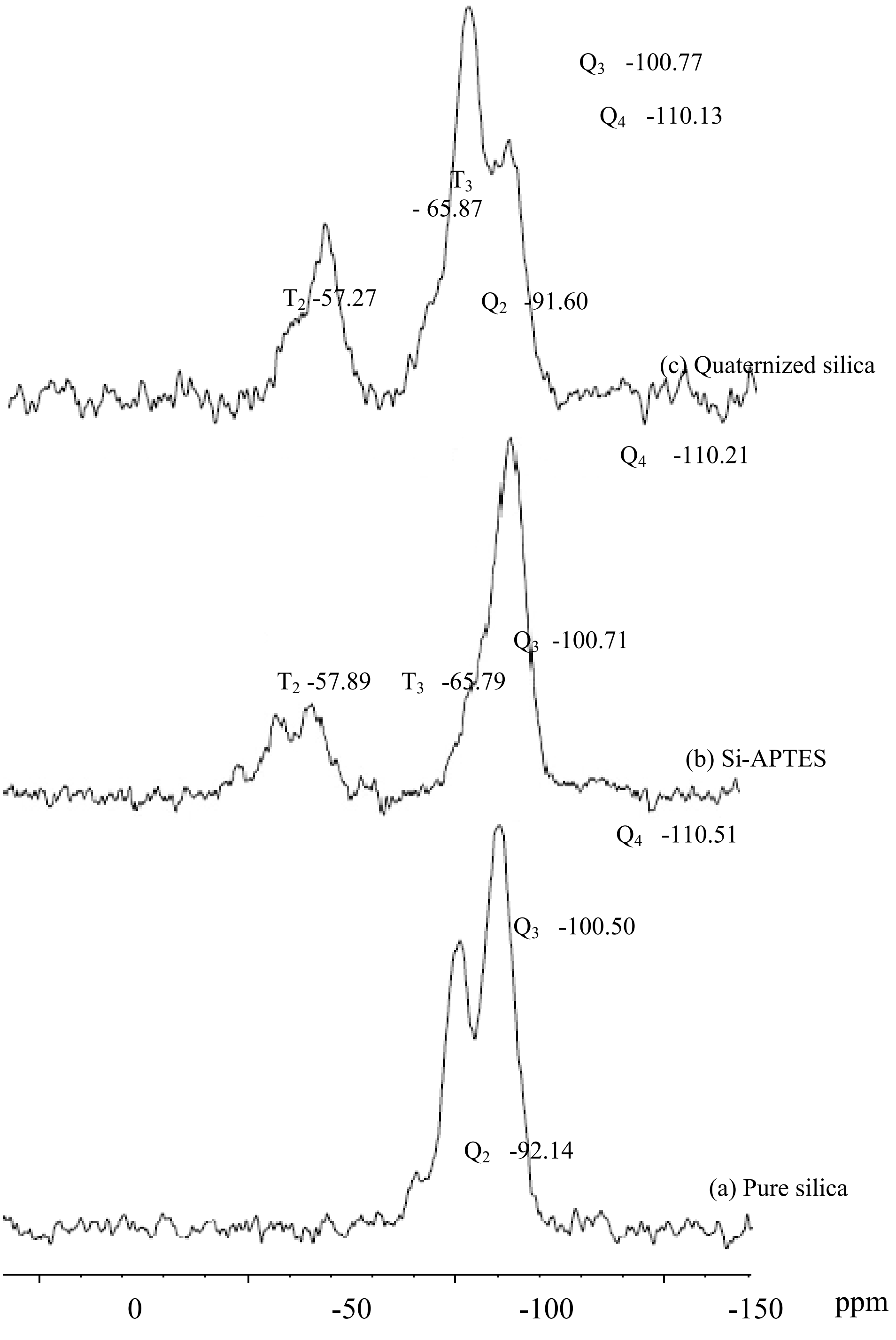


Figure 4.7. ^{29}Si NMR spectra of pure silica, Si-APTES and quaternized silica.

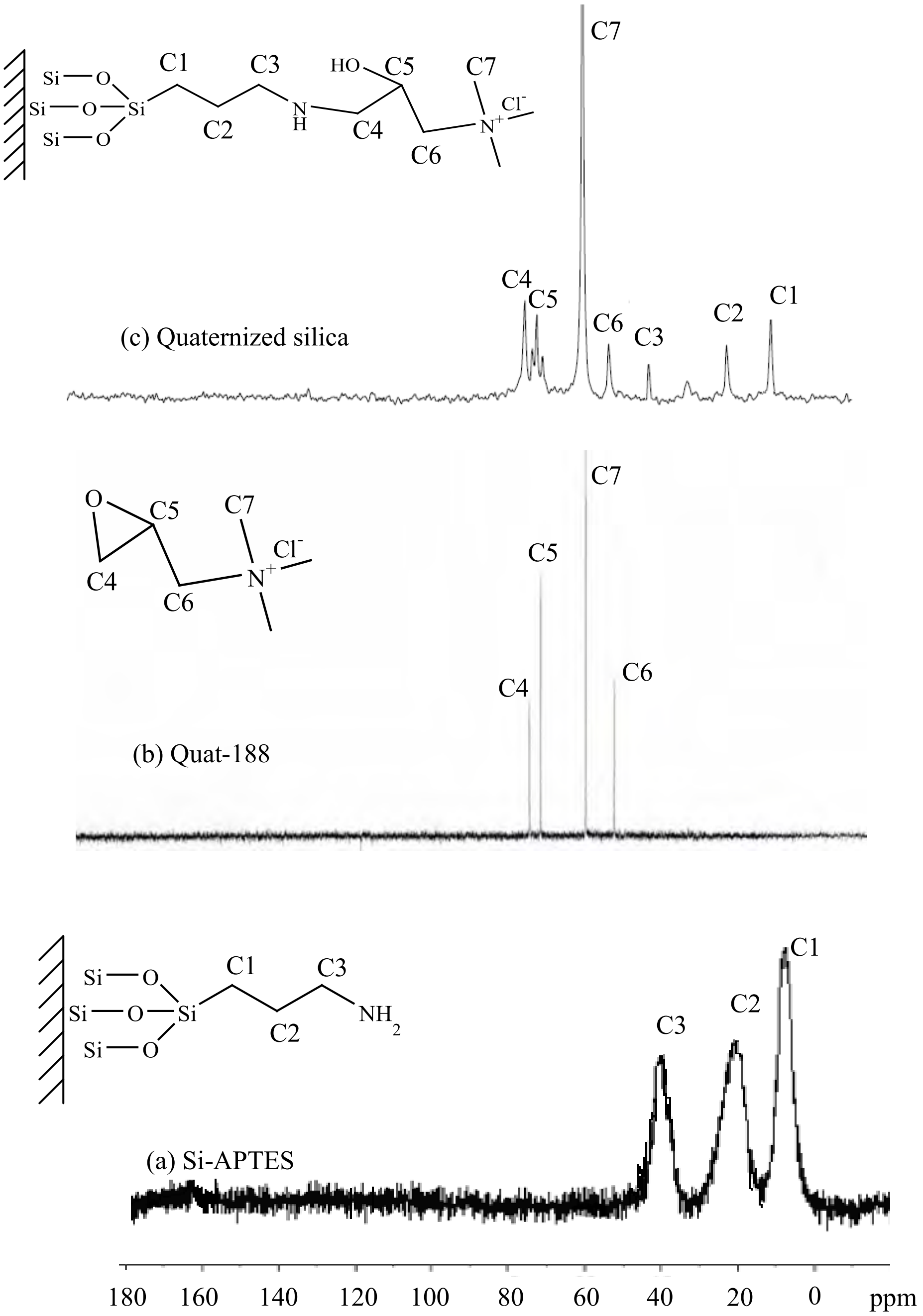


Figure 4.8. ^{13}C NMR spectra of Si-APTES, Quat-188 and quaternized silica particles and proposed structures.

Figure 4.8 showes the ^{13}C NMR spectra of Si-APTES, Quat-188 and quaternized silica, together with the proposed structure and corresponding signal assignments. Figure 4.8(c) shows the ^{13}C NMR spectrum and expected structure of quaternized silica. The spectrum has 7 signals at 9.02 ppm (C1), 20.78 ppm (C2), 39.62 ppm (C3), 47.65 ppm (C6), 55.37 ppm (C7), ~ 66.41 ppm (C5) and 69.32 ppm (C4). The ^{29}Si NMR analysis confirmed that epoxide groups have been covalently bonded to the Si-APTES. The spectrum of quaternized silica showed additional signal towards 30.01 ppm. These one signal could result from a possible disturbance of the surrounding atoms [29].

4.1.2.3 Mechanical Properties

4.1.2.3.1 Silanol concentration & amount of incorporated Quat-188

Table 4.1. Silanol concentration and amount incorporated Quat-188 with amount of 2,3-epoxypropyl trimetyl ammonium chloride.

Sample	2,3-epoxypropyl trimethyl ammonium chloride		Silanol concentration	Amount of incorporated Quat-188	Conc. of Quat-188(titration curve)
(No.)	(ml)	(10^{-2}mol)	(mmol/g)	mmol/g	(M)
1	25	6.68	1.73	0.37	0.0027
2	35	9.34	1.91	0.51	0.0042
3	45	12.01	2.00	0.73	0.0057
4	55	14.68	2.01	0.73	0.0059
5	65	17.35	2.01	0.78	0.0062
6	-	-	1.30	-	

Table 4.1 illustrats the trends of silanol concentration on increasing amount of 2,3-epoxypropyl trimethyl ammonium chloride. Silanol concentration of quatenized silicas (No.1-5) were more increased than Si-APTES (No.6) due to water in Quat-188 hydrolyzed OH group on silica surface. Silanol concentration was determined by titration with aq. HCl. In the case, Quaternization of Quat-188 on silica was determined by titration with $AgNO_3$ solution. Table 4.1 exhibited that the amount of Quat-188 incorporated on silica Quat-188 depended on the added Quat-188 in the reaction mixture.

4.1.2.3.2 Differential scanning calorimetry (DSC)

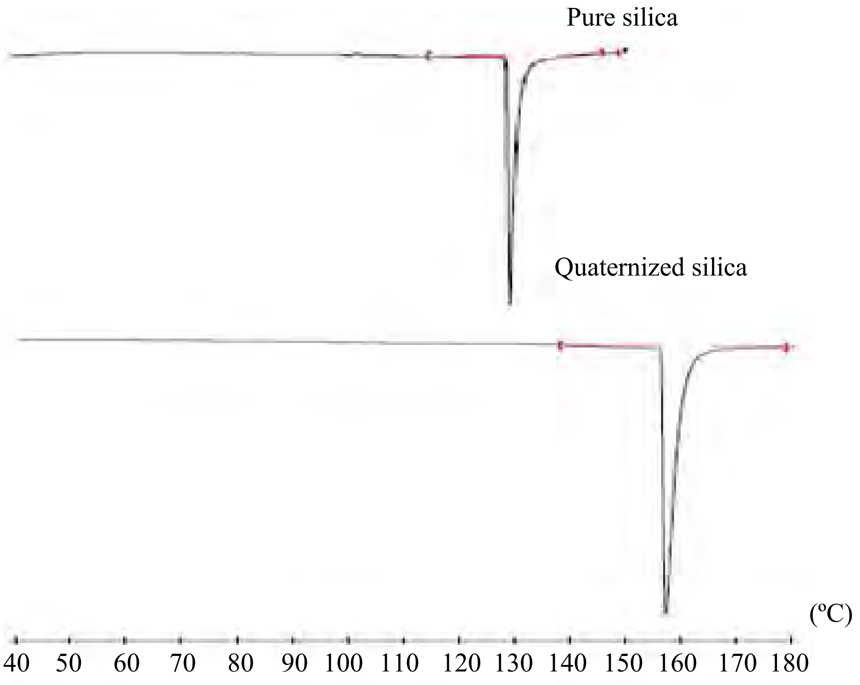


Figure 4.9. DSC thermogram of pure silica and quaternized silica particles

Figure 4.9 shows the melting temperature (T_m) of pure silica and quaternized silica (No.3) can be carefully measured using DSC instrument. The melting temperature (T_m) of quaternized silica (154.89ºC) was higher than that of pure silica (129.38ºC) which indicates that the mobility of the polymer chains was restrained by the addition of silica particles.

4.1.3 Antibacterial activitity

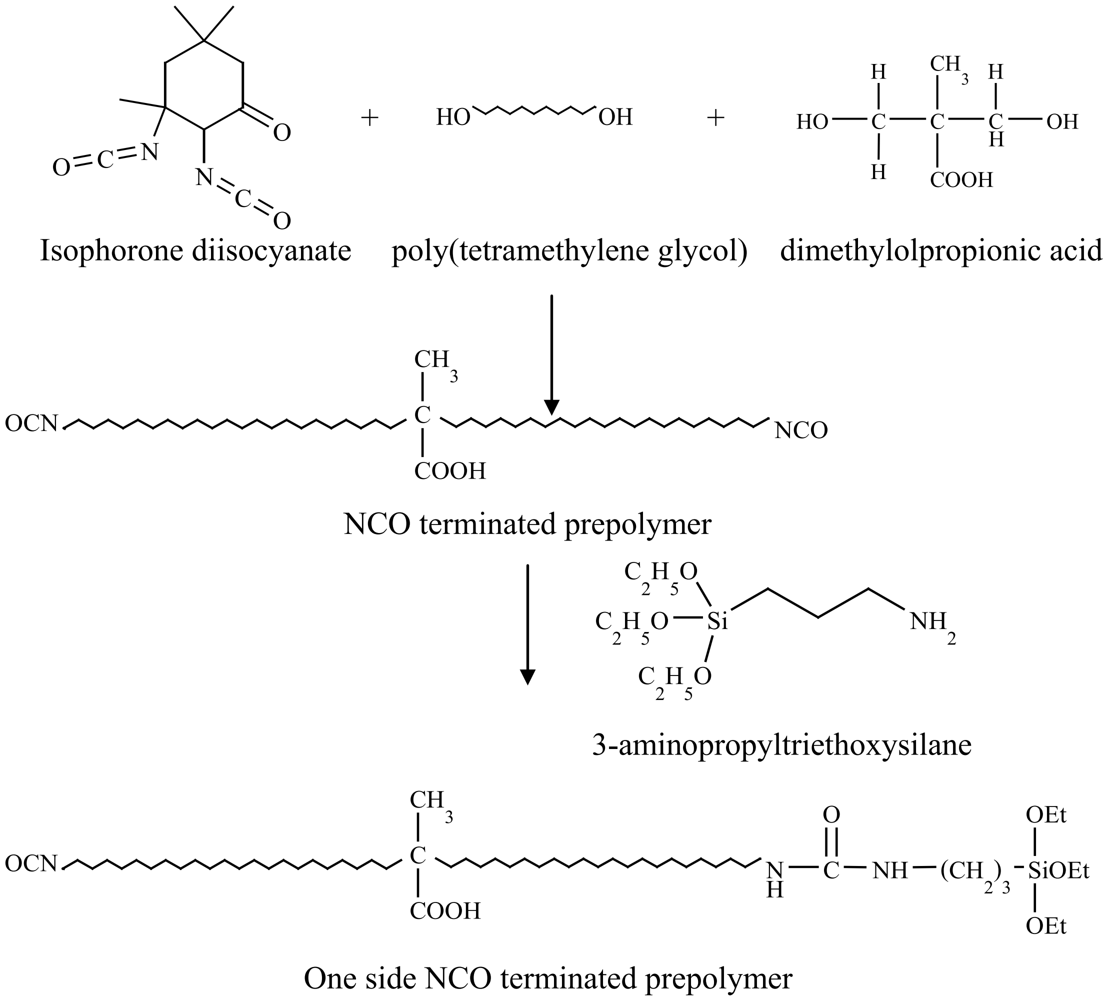
Table 4.2. Antibacterial activity of quaternized silica after exposure 24 h.

Microorganisom	Average bacterial count of control group	Average bacteriostatic rate(R%)				
		Quaternized silica (no. of sample)				
		1	2	3	4	5
E.coli(x10^5)	25.4	39.6	52.8	66.1	66	66.2
S.aureus(x10^7)	21.1	51.3	65.2	71.3	71.4	71.2

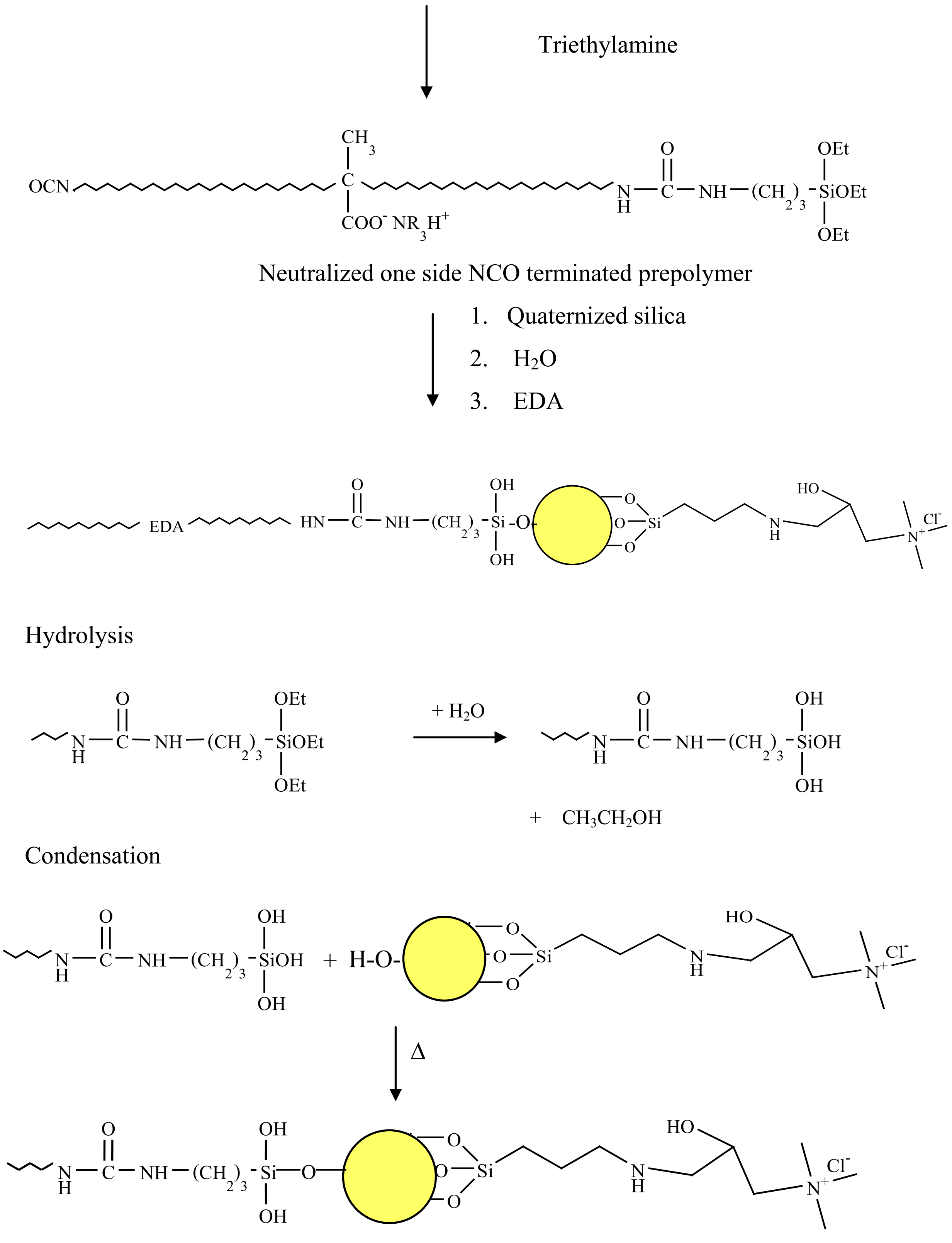
Table 4.2 exhibits the antibacterial activity of quaternized silica comparing to Quat-188. The results showed that quaternized silica had antibacterial ratio of inhibiting the growth of both *S.aureus* and *E.coli* similar to Quat-188. However, quaternized silica showed antibacterial activity against *S.aureus* higher than *E.coli*. The difference in activity against these two types of bacteria can be attributed to structural and chemical compositional differences of the cell surfaces. Gram-positive bacteria typically have one cytoplasmic membrane and thick wall composed of multilayers of peptidoglycan. However, gram-negative bacteria have more complex cell wall structure, with a layer of peptidoglycan between outer membrane and cytoplasmic membrane [30]. Quaternized silica (Sample no. 3) showed that the best of against both bacteria and this amount was selected to prepare waterborne polyurethane containing quaternized silica.

4.2 Synthesis and characterization of waterborne polyurethane containing quaternized silica.

The synthesis of the waterborne polyurethane is shown in Scheme 4.3. waterborne polyurethane was prepared by prepolymer mixing process. Firstly, polyester polyol was reacted with isophorone diisocyanate to form polyurethane prepolymer. Then dimethylolpropionic acid in *N*-methyl-2-pyrrolidone was added to the mixture. The reaction gave the prepolymer containing pendant acid group. 3-aminopropyltriethoxysilane (APTES) as a coupling agent was added and was neutralized with triethylamine to form self ionic emulsifier. Next quaternized silica was added in prepolymer polyurethane and then was dispersed in the water. Afterwards, the chain extension step was accomplished by the addition of ethylene diamine to the waterborne prepolymer dispersion.



Scheme 4.3. Synthesis of waterborne polyurethane containing quaternized silica



Scheme 4.3(cont.). Synthesis of waterborne polyurethane containing quaternized silica.

4.2.1 FTIR analysis

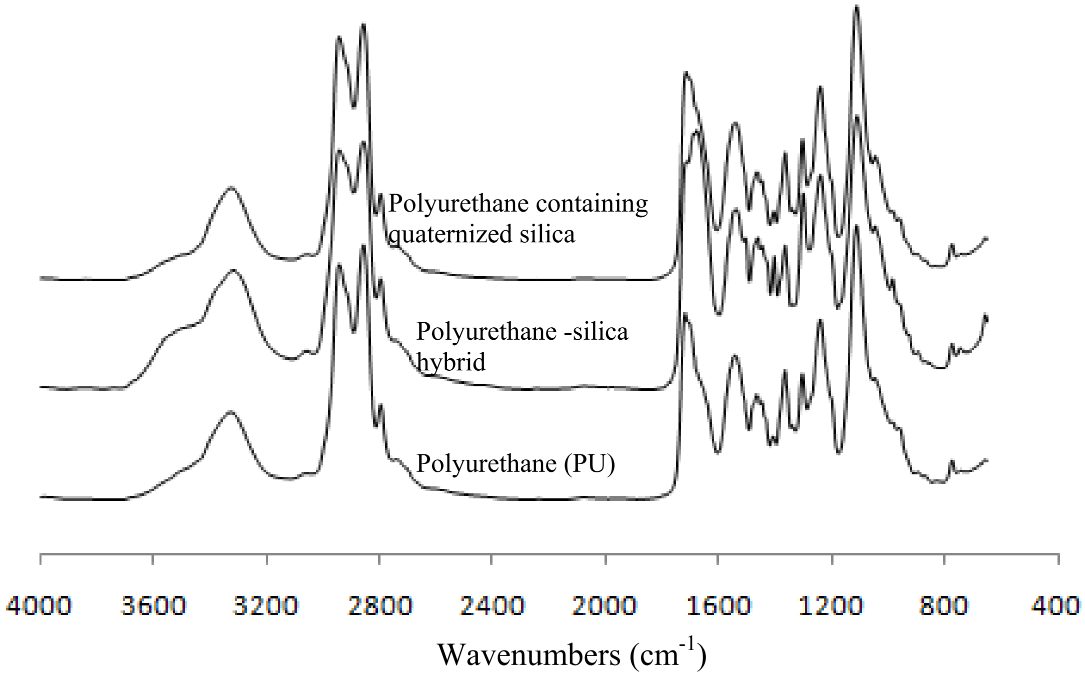


Figure 4.10. The FTIR spectra of waterborne PU, PU-silica hybrid and PU containing quaternized silica.

The absorption spectra of the NCO group (2270 cm^{-1}) of PU prepolymers disappears during the capping reactions of NCO groups with APTES on one terminal, and coupling by EDA. The results indicate that NCO groups of the PU prepolymer have completely been reacted with the amine groups in APTES and EDA [13].

4.2.2 NMR analysis

4.2.2.1 ^{29}Si solid state NMR

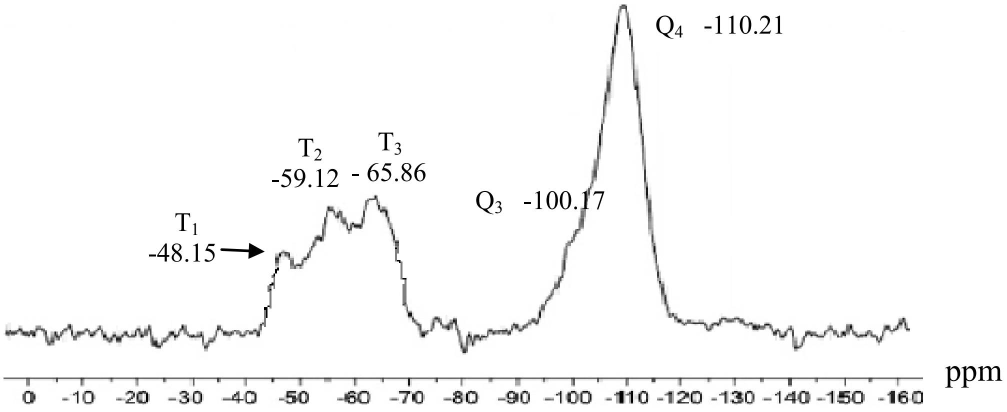


Figure 4.11. ^{29}Si solid state NMR spectrum of waterborne polyurethane containing quaternized silica.

Five signals are evident in the ^{29}Si NMR spectrum (Figure 4.11), at approximately -48.15, −59.12, −65.86, −92.56, -100.17 and −110.21 ppm, respectively. The signal at 48.15 ppm, −59.12 ppm and -65.86 ppm were assigned to T_1, T_2 and T_3 species, they represent silicon atoms with one, two and three siloxane linkages, respectively. Also, the signal at −92.56, -100.17 and −110.21 ppm is for silica particle. There is no evidence of any further signals associated with T_0 ($RSi(OH)_3$) at −40 ppm species indicating that condensation reactions have proceeded rapidly and almost completely. Because the APTES monomer has three ethoxy groups it can, in principle, form 100% T_4 species when it is fully condensed. TEA and EDA in PU structure are basic in nature and the increase in pH on their addition would be expected to accelerate the condensation reactions of the silanol groups [13,27].

4.2.3 Mechanical properties

4.2.3.1 Thermogravimatric analysis (TGA)

Table 4.3. Thermal characteristics data of silica and waterborne polyurethane before and after modified silica.

Sample	Decomposition	Temperature range (˚C)	Weight loss (wt%)	Residue (wt%)
Waterborne polyurethane (No.4)	1	30-130	21.66	
	2	130-210	33.19	
	3	210-260	4.67	
	4	260-320	3.42	
	5	320-390	9.93	
	6	390-500	26.71	0.15
Waterborne PU-silica hybrid (No.7)	1	30-170	45.20	
	2	170-260	7.26	
	3	260-330	3.62	
	4	330-390	11.91	
	5	390-510	30.10	1.65
Waterborne PU containing quaternized silica(No.8)	1	30-170	47.41	
	2	170-260	7.12	
	3	260-310	2.17	
	4	310-370	14.02	
	5	370-540	26.91	1.98

Table 4.3 showed thermal characteristics data of waterborne polyurethane, PU-silica hybrid and polyurethane containing quaternized silica. Waterborne polyurethane, PU-silica hybrid and polyurethane containing quaternized silica showed six, five and five weight loss steps, respectively. Temperature range 30-260º C of waterborne polyurethane, PU-silica hybrid and polyurethane containing quaternized silica total weight loss observed was about 59.53%, 52.46% and 54.53%, respectively. The results show that thermal resistance is enhanced with silica and quaternized silica. Temperature range 0-250ºC showed water and low-molecular polymer in the copolymers become volatile with increasing of temperature. The band of –C–N of amide group is broken at 300 ºC and the band of –COH, –CO–CO–, $–CH_2–CH_2–$ and

–CH_2–NH_2– are broken at 400 ºC [30]. Temperature higher 500ºC showed inorganic material in waterborne polyurethane.

4.2.3.2 Transmission electron microscopy (TEM)

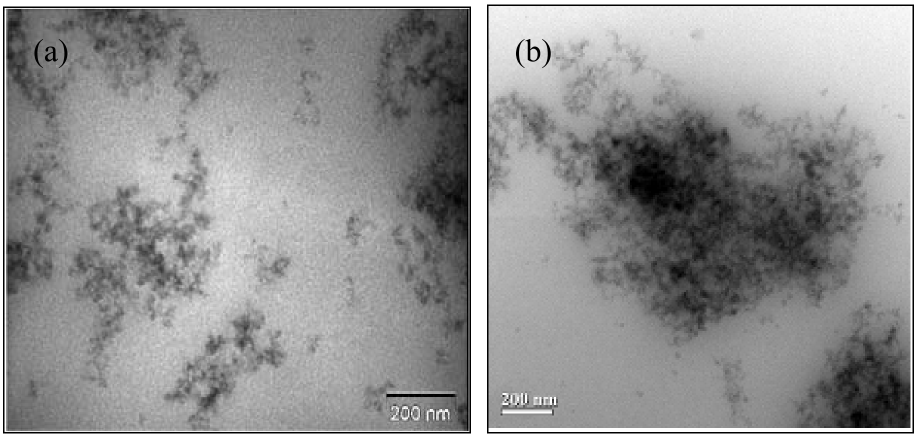


Figure 4.12 Transmission electron microscope images of (a) polyurethane-silica hybrid and (b) polyurethane containing quaternized silica

Figure 4.12 showed the transmission electron micrograph of polyurethane-silica hybrid and polyurethane containing quaternized silica. Polyurethane-silica hybrid and polyurethane containing quaternized silica were showed the silica aggregated particles extended within the polyurethane. Polyurethane containing quaternized silica was more aggregate than polyurethane-silica hybrid.

4.2.3.3 Hardness of film

Table 4.4. Hardness of waterborne polyurethane containing quaternized silica films.

	Sample					
	PU4	PU5	PU6	PU7	PU8	PU9
Appearance of film	soft	soft	hard	hard	hard	hard
Pencil Hardness test (ASTM D-3363)	2B	HB	2H	2H	2H	3H

The results of pencil hardness test on the clear waterborne polyurethane film were summarized in Table 4.4. Sample PU6 to PU9 were showed, the pencil hardness increased with silica content. Addition of silica to polyurethane makes coating harder which is likely due highly crosslinked siloxane (Si–O–Si) network within the coating. In the case for PU4 to PU6, the pencil hardness increased with the NCO/OH ratios. Significant improvement in hardness was observed for PU9 with pencil hardness about 3H.

4.2.4 Antibacterial activitity

Table 4.5. Antibacterial activity of waterborne polyurethane containing quaternized silica after exposure 24 h.

Microorganism	Average bacterial count of control group	Average antibacterial ratio (R%)				
		PU containing quaternized silica (no. of sample)				
		PU4	PU8	PU9	PU10	PU11
E.coli(x10^5)	19.3	0	7.6	16.5	23.3	32.6
S.aureus(x10^6)	24.7	0	15.1	23.8	32.7	41.2

Antibacterial activity of waterborne polyurethane containing quaternized silica films with different quaternized silica contents was tested using *E. coli* and *S. aureus* in comparison with the pure waterborne polyurethane film, as displayed in Table 4.5. It can be seen that the antibacterial ratio increased with increasing suspension concentration of antibacterial agent. The antibacterial effect of the composites on *S. aureus* is stronger than on *E. coli*.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

A series of waterborne polyurethane containing quaternized silica was successfully synthesized. Firstly, quaternized silica was prepared from Si-APTES with Quat-188 and stabilized temperature at 50ºC for 24 h. Quaternized silica was washed several time to remove unreacted Quat-188, that is critical parameter on characterize the chemical structure of quaternized silica. The second, synthesis of waterborne polyurethane was observed, since the water addition rate is a critical parameter to obtain a stable emulsion, water was fed for 20 min at constant flow rate. And 25 ml of NMP was added for adjust viscous in system. These method had easily to prepare, good film forming and good stability. When the NCO/OH ratio and the amount of quaternized silica in the reaction increased, polyurethane containing quaternized silica exhibited higher film hardness. The addition of quaternized silica in the reaction was limited at 4 phr of the total solid of waterborne polyurethane due to the high viscosity of the mixture. Quaternized silica and waterborne polyurethane containing quaternized silica showed antibacterial activity against *S.aureus* and *E.coli* and good mechanical properties.

Further Work

In this work, the amount of incorporated Quat-188 on silica surface was the one of the factor that affected the antibacterial activity. Therefore, the effect of amount of incorporated Quat-188 on silica surface shall be studied by vary method & type of quaternary ammonium salt.

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Appendices

Appendix A

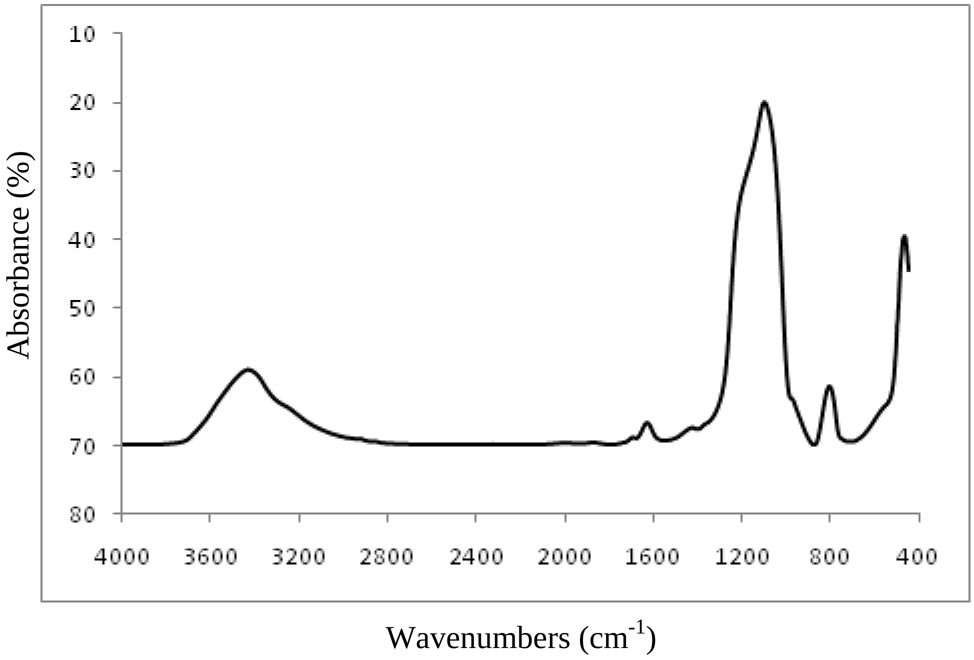

Figure A.1. FTIR spectrum of pure silica.

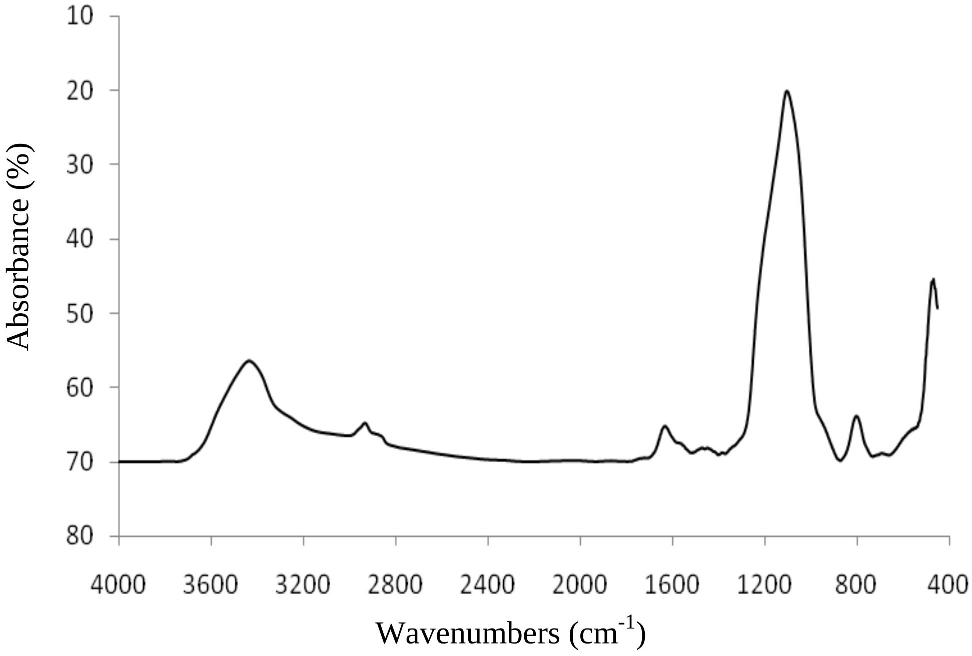

Figure A.2. FTIR spectrum of Si-APTES.

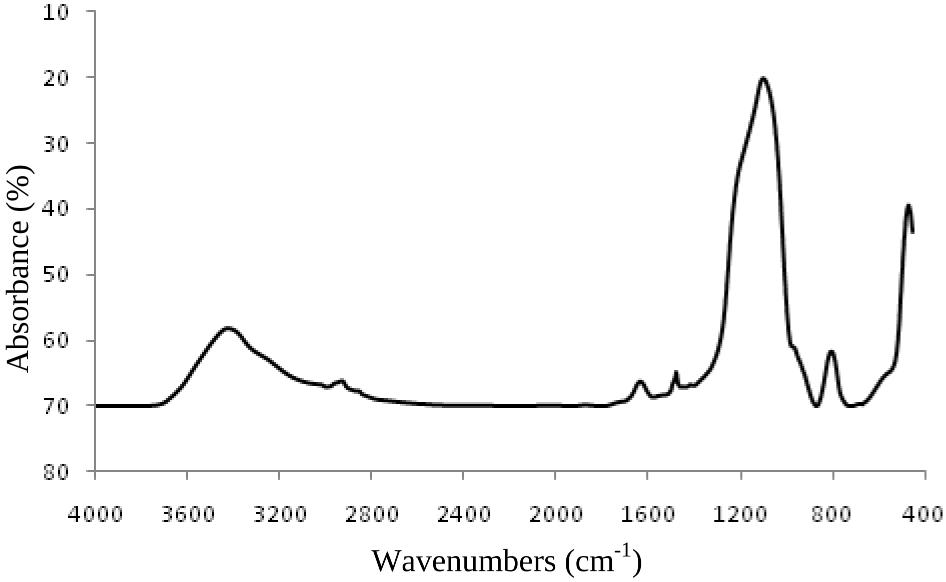

Figure A.3. FTIR spectrum of quaternized silica.

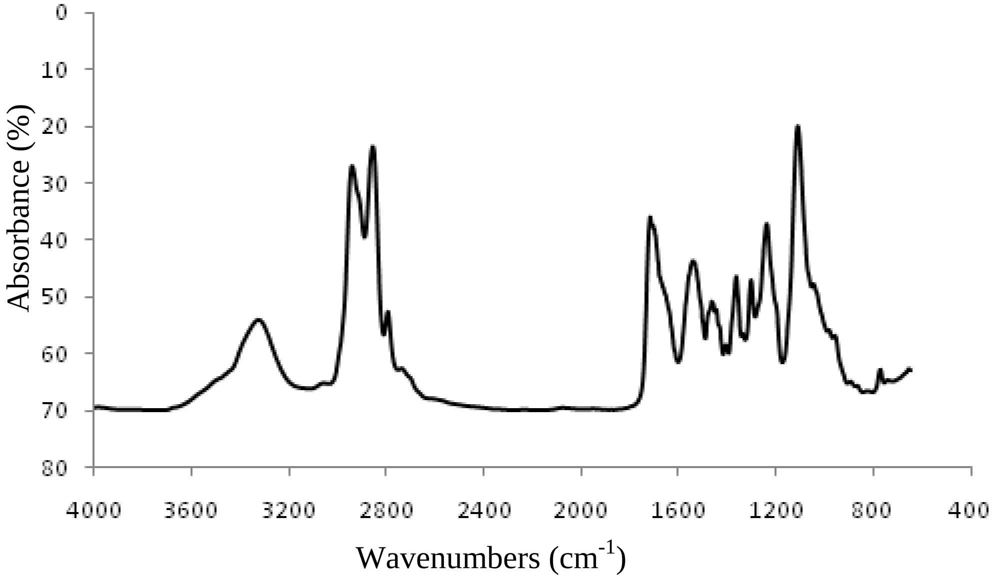

Figure A.4. FTIR spectrum of pure waterborne polyurethane.

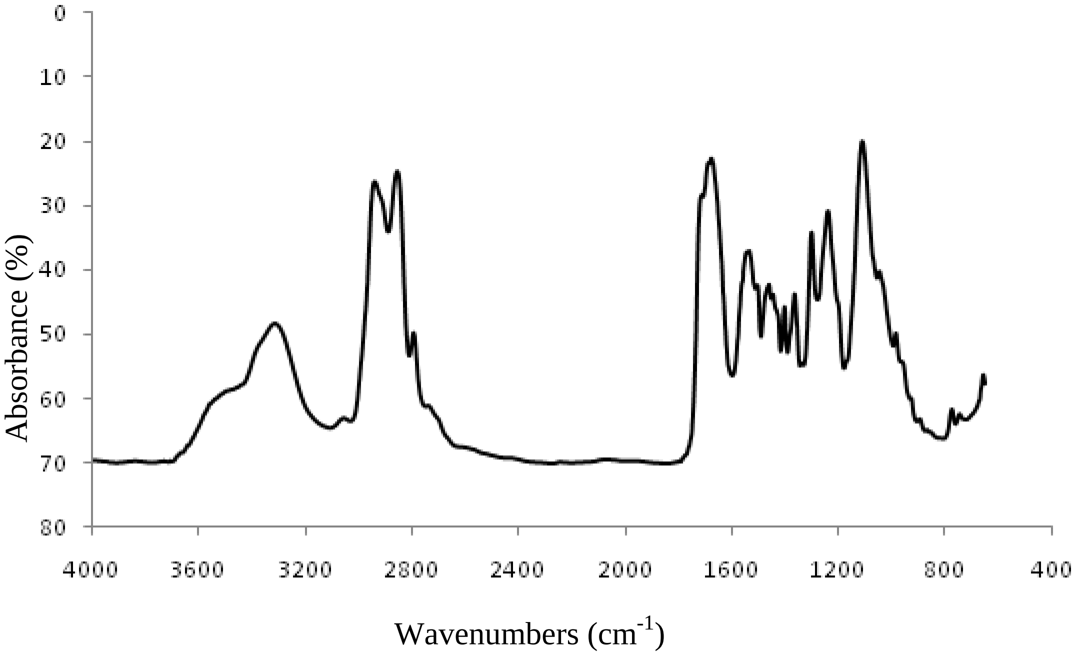

Figure A.5. FTIR spectrum of waterborne polyurethane-silica hybrid.

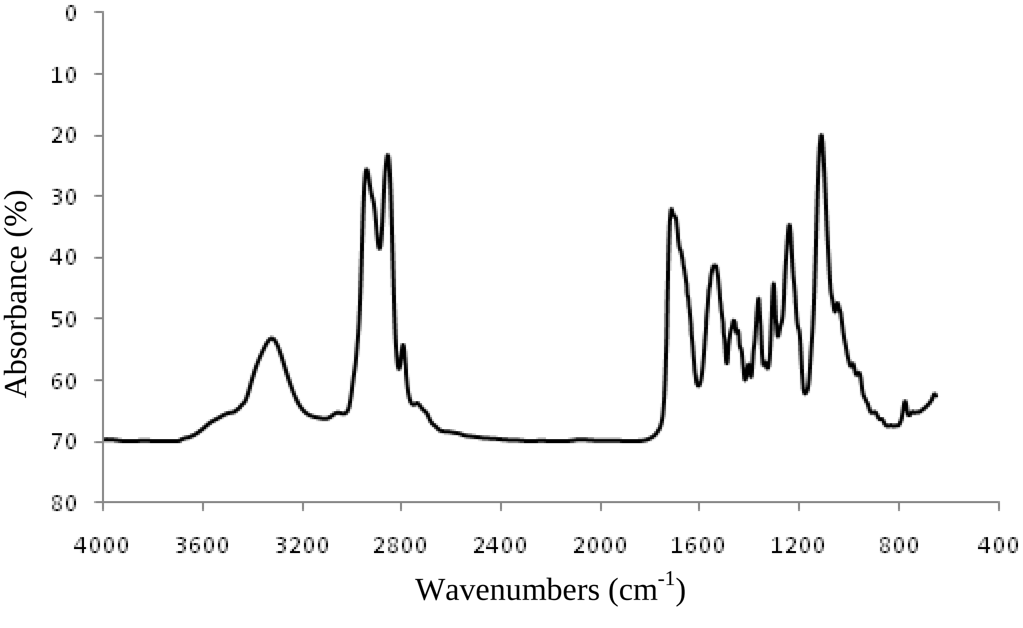

Figure A.6. FTIR spectrum of waterborne polyurethane containing quaternized silica hybrid.

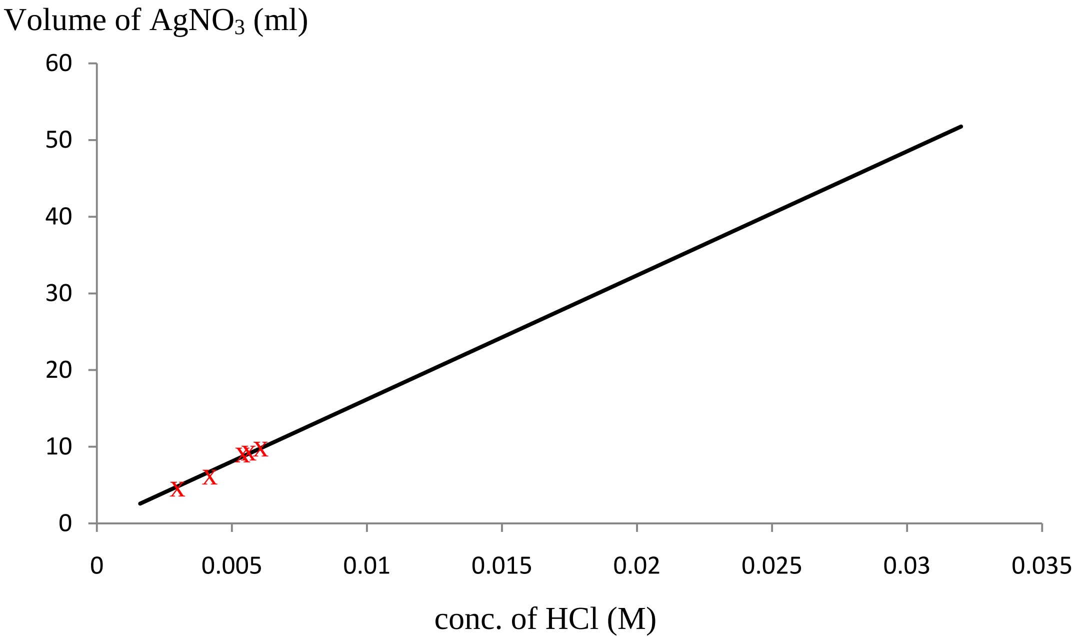

Figure A.7. Titration curve of concentrate of HCl(M) with volume of $AgNO_3$(ml)

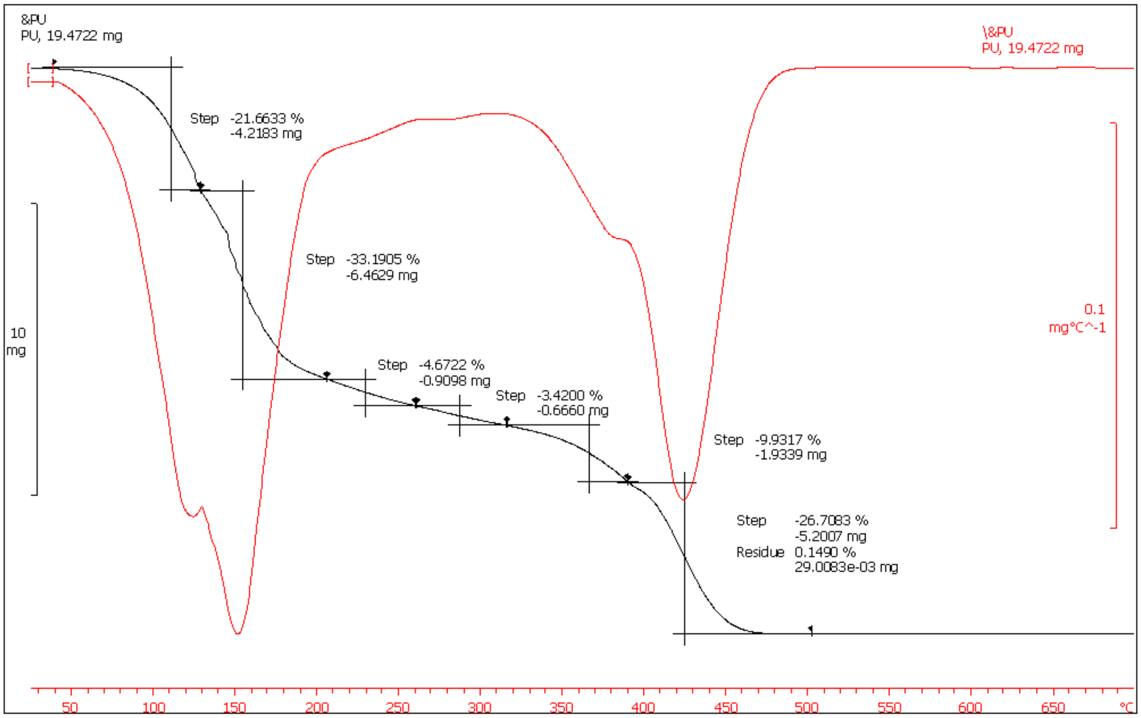

Figure A.8. TGA curves of waterborne polyurethane

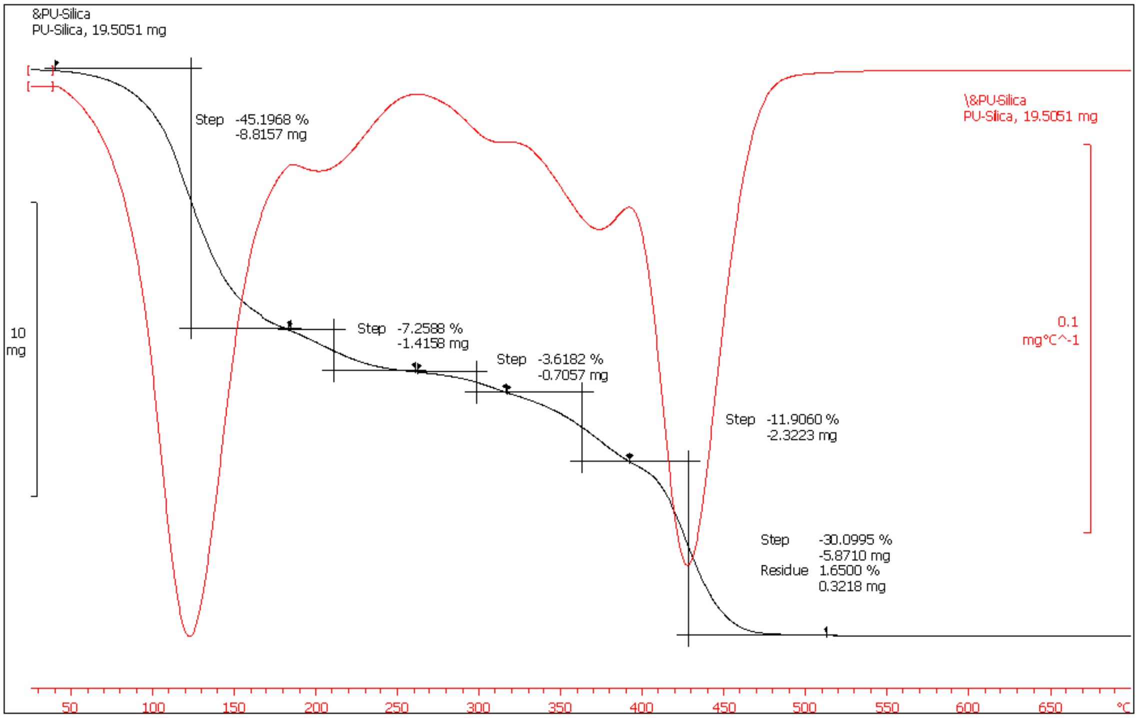

Figure A.9. TGA curves of waterborne polyurethane-silica hybrid

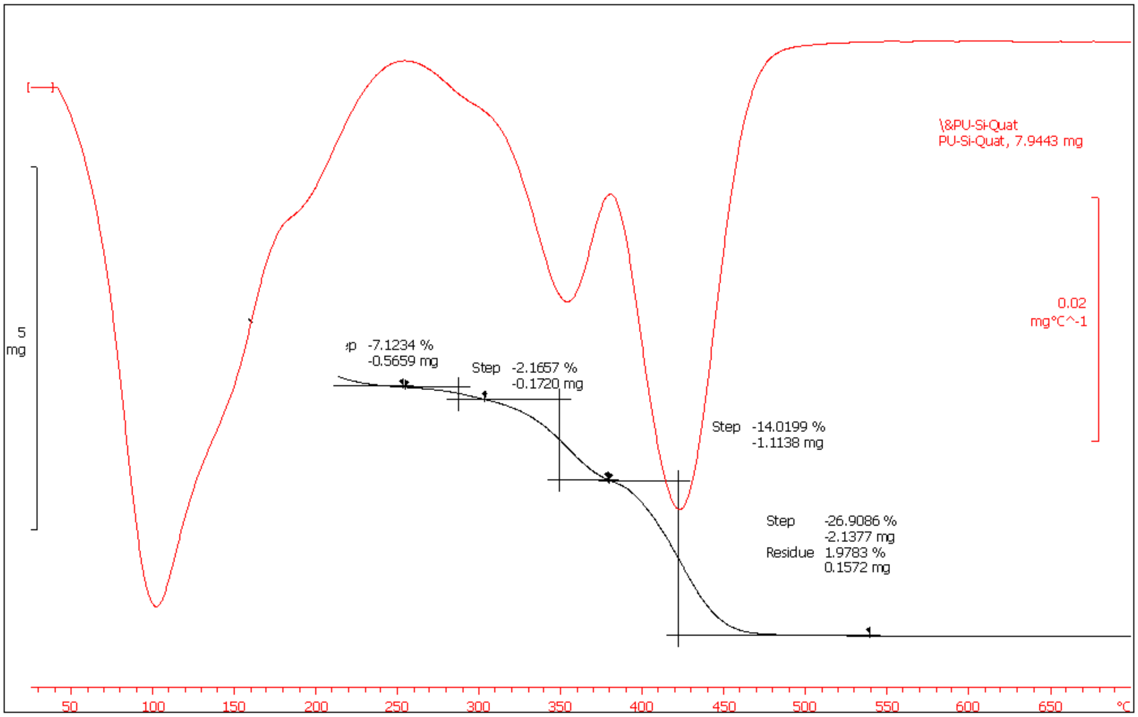

Figure A.10. TGA curves of waterborne polyurethane containing quaternized silica

Appendix B

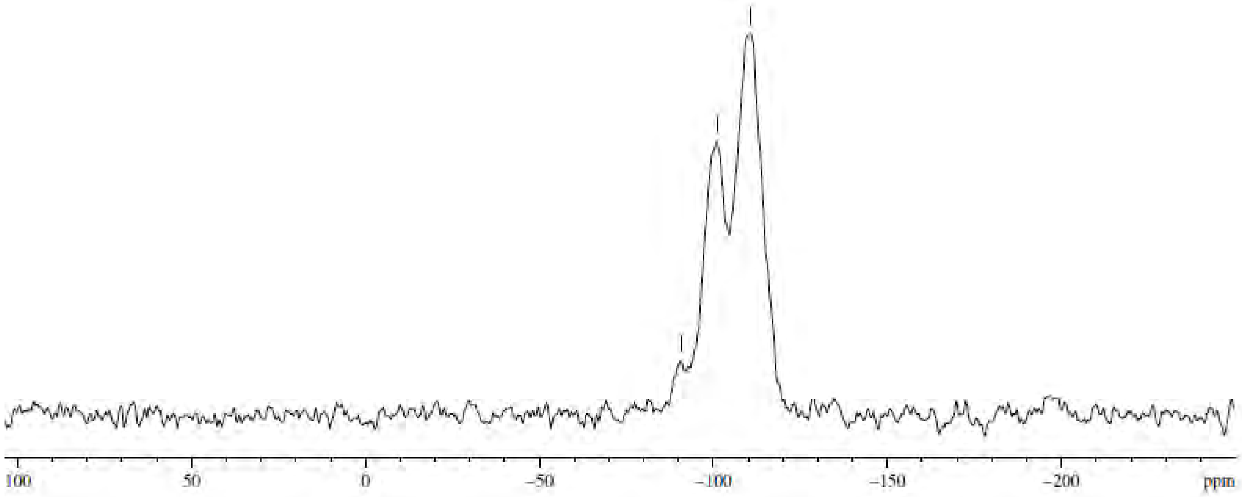

Figure B.1. ^{29}Si NMR spectrum of pure silica

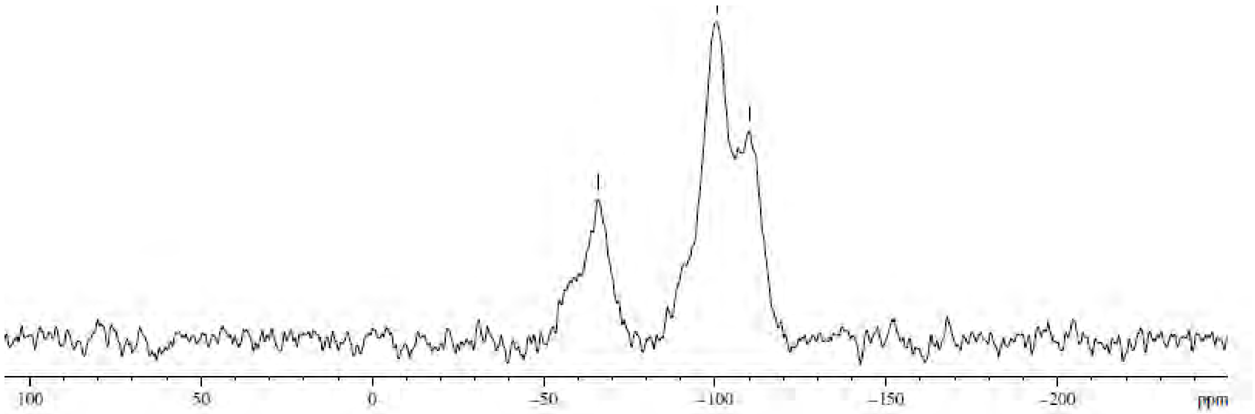

Figure B.2. ^{29}Si NMR spectrum of Quaternized silica

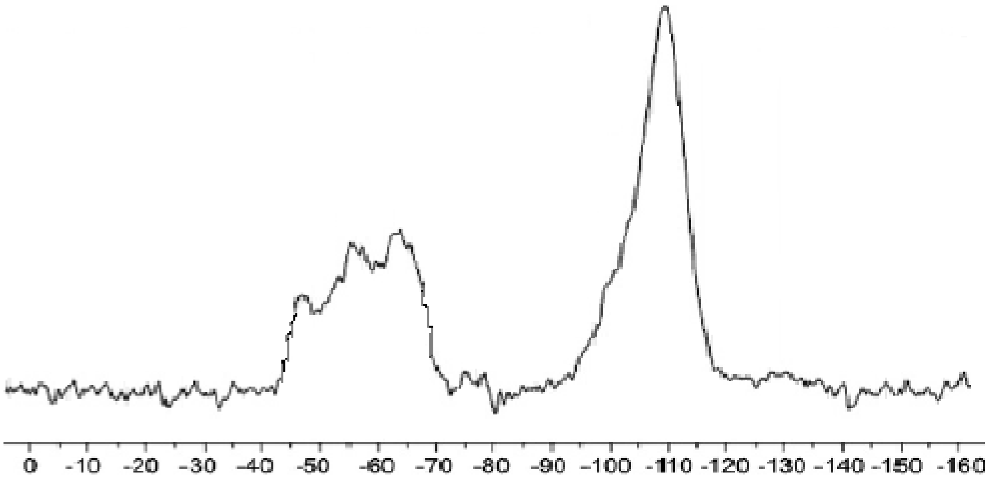

Figure B.3. ^{29}Si NMR spectrum of waterborne polyurethane-quaternized silica hybrid

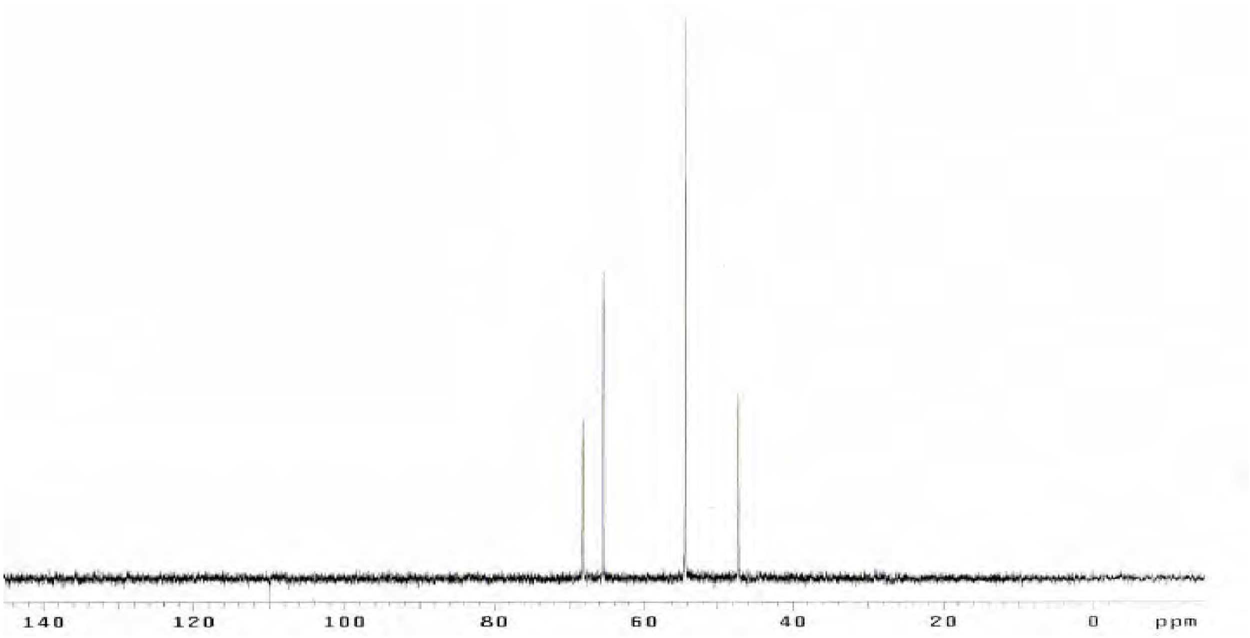

Figure B.4. ^{13}C NMR spectrum of Quat-188

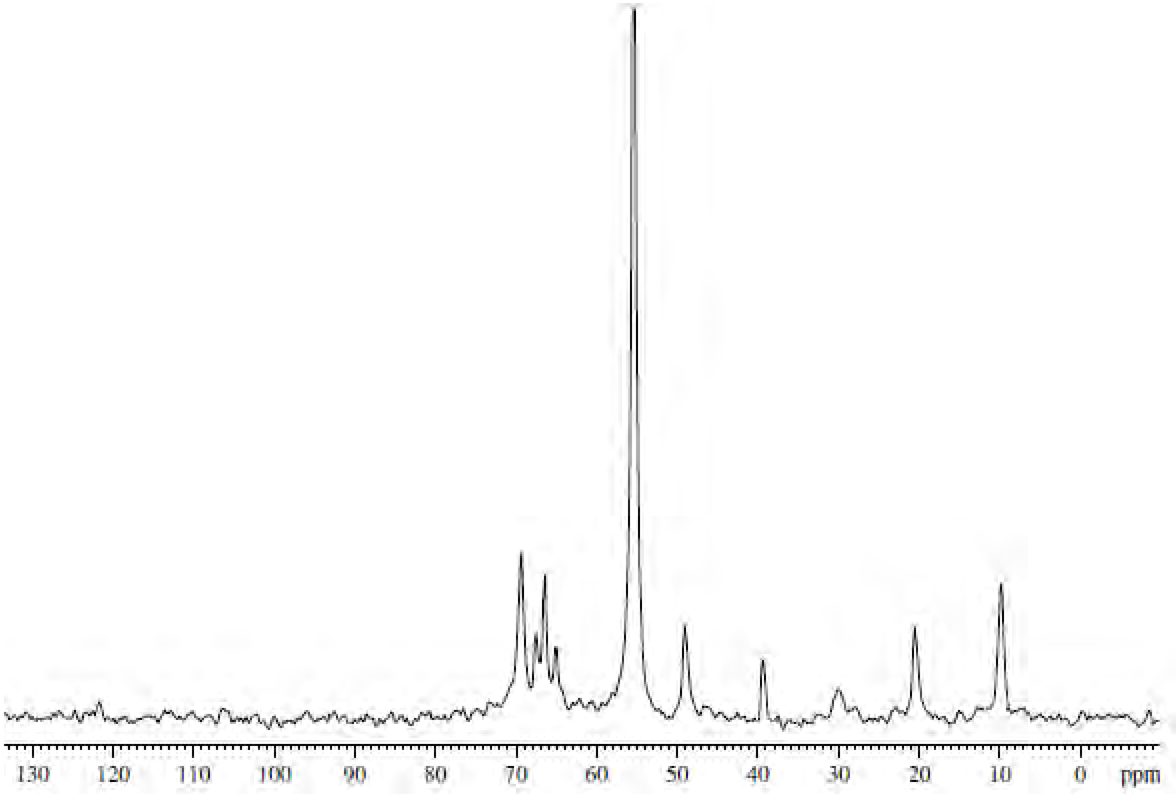

Figure B.5. ^{13}C NMR spectrum of waterborne polyurethane-quaternized silica hybrid

VITAE

Mr.Sumet Lertpanyachokchai was born in 1979 at Bangkok, Thailand. He got a Bachelor’s Degree of Science in Chemistry from King Mongkut’s Univesity of Technology Thonburi in 2003. After that, He worked at TOA Paint (Thailand) Co;Ltd until 2007 he started his graduate study a Master’s Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed the program in 2009.