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STUDY ON CHITOSAN THIN FILM FOR VAPOUR

SENSOR APPLICATION

by

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In the name of Allah the Most Gracious and The Most Merciful.
With the Selawat and Salam to Prophet Mahammad SAW.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C	Degree Celsius
AFM	Atomic Force Microscopy
C_2	Carbon 2
C_3	Carbon 3
C_6	Carbon 6
cc	Concentration
C_7H_8	Toluene
CEAT	Contaminated air exposure technique
$CH_2 (CH2CHO)_2$	Glutaraldehyde
CH_3	Methyl
CH_3CH	Methanol
CH_3COOH	Acetic acid
CH_4O	Methanol
CPs	Conducting polymers
CS	Chitosan
Cu	Copper
DA	Degree of acetylation
DC	Direct currant
DD	Degree of deacetylation
DI	Distilled water
FTIR	Fourier Transform Infra-Red
g	Gram
H	Hydrogen
H_2O	Water
Hz	Hertz
ICP	Intrinsically conducting polymer

IUPAC	International Union of Pure and Applied Chemistry
Kg	Kilogram
kV	Kilovolt
M	Molarity
m^3	Meter Cubic
MOS	Metal-Oxide Semiconductor
NH_2	Amino group
NH_3^+	Amine
nm	Nanometer
O	Oxygen
OH	hydroxyl group
PCB	Printed Circuit Board
pH	The concentration of hydrogens ions
RA	Roughness area
RMS	Root mean square
Sec	Second
SEM	Scanning Electron Microscope
SnO_2	Tin dioxide
V	Volt
w/v	Concentration
α	Alpha
β	Beta

KAJIAN TENTANG FILEM NIPIS KITOSAN UNTUK APLIKASI PENGESAN WAP

ABSTRAK

Tujuan projek ini ialah untuk menganalisis sifat-sifat elektrik pengesan filem kitosan nipis apabila didedahkan kepada air, metanol dan toluena. Filem kitosan terbukti berpotensi sebagai pengesan yang berjaya mengesan metanol dan toluena. Pendedahan metanol dan toluena dengan empat kepekatan 0.1, 0.5, 1.0 dan 2.0cc dalam kitosan adalah untuk mengkaji kadar kepekaan dan pemilihan pengesan filem kitosan kepada metanol, toluena dan air. Kaedah pemendapan elektrokimia telah dipilih sebagai cara untuk mereka filem kitosan. Ujian elektrik telah dijalankan untuk mengkaji sifat-sifat pengesan seperti kepekaan, masa bertindak balas, pemulihan, kestabilan, pengulangan, pemilihan dan kebolehulangan telah dijalankan untuk memenuhi keperluan filem pengesan kitosan sebagai pengesan yang dipercayai. Ujian pencirian yang merangkumi Mikroskopi Daya Atom (AFM), Mikroskopi Penskanan Elektron (SEM) dan Fourier Transform Inframerah Spektrometri (FT-IR) telah dilakukan untuk mengkaji struktur mikro pengesan filem kitosan. Daripada keputusan, kepekatan terbaik kitosan untuk fabrikasi pengesan filem kitosan ialah 1.75 w/v%. Filem kitosan selepas didedahkan kepada metanol menunjukkan voltan keluaran yang tinggi daripada filem kitosan selepas didedahkan dengan toluena. Ini menunjukkan filem kitosan lebih peka terhadap metanol berbanding toluena. Imej SEM dan AFM filem kitosan menunjukkan permukaan padat dan licin yang menunjukkan keseragaman permukaan filem kitosan. FT-IR menunjukkan kehadiran kumpulan berfungsi yang utama pada filem kitosan sama ada sebelum atau selepas terdedah kepada metanol dan toluena. Oleh itu, filem kitosan berpotensi sebagai pengesan yang dipercayai kerana ia mempunyai kepekaan yang tinggi, tindak balas yang pantas, stabil, pemulihan yang baik, pengulangan dan pemilihan kepada air, metanol dan toluena.

STUDY ON CHITOSAN THIN FILM FOR VAPOUR SENSOR APPLICATION

ABSTRACT

The aim of this project is to analyse the electrical properties of the chitosan film sensor exposed to water, methanol and toluene. Chitosan film has proven to be potential as reliable sensor for methanol and toluene detector. The exposure of methanol and toluene with four concentrations 0.1, 0.5, 1.0 and 2.0cc into chitosan is to study the sensitivity and selectivity of chitosan film sensor upon methanol, toluene and water. Electrochemical deposition method has been chosen as a method to fabricate chitosan film. Electrical testing was done to study the sensing properties such as sensitivity, respond time, recovery, stability, repeatability, selectivity and reproducibility has been done in order to fulfill a requirement chitosan film sensor as reliable sensor. Characterization testing which include Atomic Force Microscopy (AFM), Scanning Electrons Microscopy (SEM) and Fourier Transform Infrared Spectrometry (FT-IR) has been performed to study the microstructure of chitosan film sensor. From the results, the best chitosan concentration to fabricate chitosan film sensor is 1.75 w/v%. Chitosan film after exposed to methanol shows higher output voltage than chitosan film after exposed to toluene. It indicates chitosan film is more sensitive to methanol than toluene. SEM and AFM images of chitosan films show compact and smooth surface which indicates homogeneity of chitosan film surface. FT-IR shows the presence of the domain functional group in either chitosan film before or after exposed to methanol and toluene. Thus chitosan film is potential as a reliable sensor because it has high sensitivity, rapid response, stable, good recovery, repeatable and selective to water, methanol and toluene.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Chitin and chitosan (CS) polymers are natural amino polysaccharides having unique structures, multidimensional properties, highly sophisticated functions and wide ranging applications in biomedical and other industrial areas (Pillai et al., 2009). Chitosan is a copolymer of glucosamine and N-acetylglucosamine units linked by 1, 4-glucosidic bonds, which is a similar structure to cellulose (Sang-Dong et al., 2009). Chitosan occurs naturally in some microorganisms, yeast and fungi (Yap et al., 2011). The interest in this biopolymer for electrochemical applications is due to its combination of film forming ability, high water permeability, good adhesion, biocompatibility, nontoxicity, high mechanical strength and susceptibility to chemical modifications (Martínez-Huitle et al., 2010). The primary amino group at the ring C2 position and the primary and secondary hydroxyl functionalities at the ring C6 and C3 position, respectively, are amenable to selective chemical modification to improve its solubility and other properties for medical, pharmaceutical, agricultural and technological applications (Yan-ming & Zhi-qiang, 1999).

Sensor technology is dependent on progress in materials science and technology, and every time a new material is discovered it is soon investigated for applications such as conducting polymers sensors, and solid ionic materials (Joseph et al., 2003).

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The world seems to have a natural division between physical and chemical sensors. However it is not easy to classify them, such as relative humidity sensors a chemical sensor traditionally lumped with physical sensors. Also sensors are frequently discussed along with the matter of actuators. Chemical sensors have a chemical or molecular target to be calculated. Biosensors are known as sensors that use biomolecules and structures to measure something with biological significance or bioactivity furthermore, appropriately biosensors aim a biomolecule of interest for measurement the biosensor can normally be considered a subset of chemical sensors due to the transduction methods sometimes referred to as the sensor platforms are just like those for chemical sensors. Chemical sensor arrays with instrumentation having famous names such as the electronic nose or electronic tongue have been constructed to state chemically complex analyses like taste, odor, toxicity, or freshness (George & Raeann, 2005).

Typically, electronic signal is produced by sensor, being a current voltage or impedance conductance change caused by changing analyte composition or quality. While chemical sensors having a physical transducer and a chemically sensitive layer or recognition layer the micro instrument or spectrometer sends out an energy signal it can be optical, electrical, or thermal, and reads the change in this same characteristics caused by the intervening chemical (Clark & Lyons, 1962).

Sensors are composed of an active sensing material with a signal transducer. The signal without any amplification is transmitted from a selective compound or from a change in a reaction is considered the function of these two important devices in sensors.

These devices produce any one of the signals as electrical thermal or optical output signals which could be converted in to digital signals for further processing. One of the

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ways of classifying sensors is done based on these output signals. Between these electrochemical sensors have more benefit over the others because in these the electrodes can sense the materials which are present within the host without doing any harm to the host system. Other than that, sensors can be broadly classified in to two categories as biosensors and chemical sensors (Wu et al., 2007).

The biosensors can be defined in terms of sensing aspects where these sensors can sense biochemical compounds like tissues nucleotides and even biological proteins (Wilson & Gifford, 2005 and Chen & Chzo, 2006). Within these sensors the active sensing material on the electrode should act as a catalyze and catalyst the reaction of the biochemical chemical compounds to achieve the output signals (Vasantha & Chen, 2006 & Simoyi et al., 2003). The combination of electrochemical and biosensor has given rise to a new type of sensors where the electrochemical methods are applied for the construction and working of a biosensor (Balasubramanian & Burghard, 2003 & Wang et al., 2006). The development and selection of an active substantial is a challenge. In the development of any biosensor, some critical performance requirements for a particular application must be considered. A reliable biosensor should respond selectively to an analyte of interest among a range of analytes. Alternatively, the response may be to a group of analytes of similar chemical structure such as carbonyl compounds. Apart from selectivity, a biosensor needs to show high sensitivity. The signal-to-noise ratio must be large, with detectable signals from small changes in analyte concentration (Vasantha & Chen, 2006). The linear dynamic range of the calibration curve should be wide enough for the assay of the analyte.

Polymers used in sensor devices either participate in sensing mechanism or immobilize the component responsible for sensing the analyte. A new class of polymers

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known as intrinsically conducting polymers (CPs) or electroactive conjugated polymers exhibit interesting electrical and optical properties, which were found only in inorganic systems. Electrically conducting polymers differ from all the familiar inorganic semiconductors (silicon and germanium) in two important features that polymers are molecular in nature and lack long-range order. CPs contain n-electron backbone which is responsible for their unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity, and are used to enhance speed, sensitivity and versatility of sensors. Properties of CPs depend strongly on doping level, ion size of the dopant, protonation level and water content. CPs finding ever-increasing use indiagnostic medical reasents (Heller, 1990), and with a distinguishable chemical memory are prominent new materials for the fabrication of industrial sensors. A number of reviews (Trojanowicz & Krawczyk, 1995) on the use of conducting polymers in the fabrication of sensors have been published. Sensors may be classified depending on the mode of transduction and application.

Conducting polymers (CPs) that possesses high electrical conductivity due to their π conjugated electrons are one of the more promising biocompatible materials and have been used in various applications (Malinauskas et al., 2005, Heath, 1995, Alivisatos, 1996 & Andres et al., 1996). Thus, they have been used as a transducer in biological sensors because of their attractive properties such as high stability at room temperature, good conductivity output and facile polymerization (Mala et al., 2007). Another important advantage of using CPs is that the biomolecules can be immobilized onto the nanowire structure in a single step rather than the multiple steps that are required when other non-polymeric materials are used. In addition, the electrochemically prepared CPs can be grown

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with controlled thickness using lower potential and they also have an excellent enzyme-entrapping capability (Li et al., 2005, Malhotra et al., 2006, Rajesh, 2004 & Yamato & Kaneto, 2006).

Electrochemical deposition is used in the manufacturing of products for our daily lives it is a process by which a film of solid metal is deposited from a solution of ions onto an electrically conducting surface. Many times, the deposited film has dimensions within the nanoscale and hence the resulting product has gone through a process of nanomanufacturing. There are some advantages using electrochemical deposition method. This is because compare to the other methods, this method offers the advantages of higher deposition rate, shorter processing time and possibility to control the thickness of the chitosan film. The surface of the material will not damage if this method is used.

In this study, chitosan has been used as a sensing material to fabricate the chitosan film sensors in order to detect the present of methanol and toluene in air.

1.2   Problem Statement

Chitosan is a natural polymer that has very good properties as a sensor material. Chitosan film has potential in pharmacy or for the conducting biomaterials application because the presence of large groups of amino (-NH_2) and it has hydroxyl group (-OH-) in molecule that can interact with water molecule. Providing active bonding sites to interact with the other chemical elements. However, films that made only from chitosan are low in water resistance and potential to be swelling. Methanol and toluene are harmful to human body. From this reason, electrochemical deposition technique is the suitable operation method for chitosan film sensor.

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1.3   Research Objectives

1.3.1   To study the effect of chitosan concentrations to the electrical properties of chitosan film.

1.3.2   To study the sensing properties of chitosan film sensor upon water, methanol and toluene.

1.3.3   To study the microstructure of chitosan film sensors.

1.4   Scope of the Research

In this project, the different chitosan concentrations have been used to study the effect of chitosan concentrations towards the electrical properties of the chitosan films.

At first, this study was focused on fabrication of chitosan film sensor then the electrical properties of the chitosan films. The last part of this study was the characterization of the microstructure of chitosan film. The chitosan films have been produced using an electrochemical deposition method. The chitosan films have been used to study the effect of the chitosan concentration on the performance of chitosan film sensor, whereas the study of the microstructure of the chitosan films were carried out using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Fourier Transform Infrared (FTIR). The performance of the chitosan films sensor was tested based on its stability to maintain its condition when exposed at different analyte to fulfill the requirement as a reliable sensor, all sensing properties i.e. Sensitivity, response time, stability, recovery, repeatability and selectivity of the chitosan film sensor towards water, methanol and toluene have been studied.

CHAPTER 2

LITERATURE REVIEW

2.1   Chitin and Chitosan

Chitin and chitosan (CS) polymers are natural amino polysaccharides having unique structures, multidimensional properties, highly sophisticated functions and wide ranging applications in biomedical and other industrial areas (Chandy & Sharma 1990, Paul & Sharma 2000 and Muzzarelli, 2005). Being considered to be materials of great futuristic potential with immense possibilities for structural modifications to impart desired properties and functions, research and development work on chitin and CS have reached a status of intense activities in many parts of the world (Prashanth & Tharanathan, 2007, Khor 2002 and Rinaudo, 2006).

The positive attributes of excellent biocompatibility and admirable biodegradability with ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity have provided ample opportunities for further development (Mourya & Inamdar, 2008). It has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields (Hirano, 1999). With data emerging from not less than 20 books, over 300 reviews, over 12,000 publications and innumerable patents, the science and technology of these biopolymers are at a turning point where one needs a very critical look on its potential to deliver the goods (Zohuriaan-Mehr, 2005). Prior to doing so, it is necessary to overview the data emerged on one of the serious problems faced in the utilization of chitin and CS.

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2.1.1   Structures of Chitin and Chitosan

It is now well established that the difficulty in solubilization of chitin results mainly from the highly extended hydrogen bonded semi-crystalline structure of chitin (Rinaudo, 2006 & Kurita, 1998). Chitin is a structural biopolymer, which has a role analogous to that of collagen in the higher animals and cellulose in terrestrial plants (Mayer & Sarikaya, 2002). Plants produce cellulose in their cell walls and insects and crustaceans produce chitin in their shells (Muzzarelli et al, 1986). Cellulose and chitin are, thus, two important and structurally related polysaccharides that provide structural integrity and protection to plants and animals, respectively (Muzzarelli et al, 1986, Dumitriu, 1996 & Muzzarelli, 1973).

Chitin occurs in nature as ordered crystalline micro-fibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast (Rinaudo, 2008, Vincent & Wegst, 2004 & Raabe et al, 2007). In crustaceans, chitin is found to occur as fibrous material embedded in a six stranded protein helix. Chitin may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group (Rinaudo, 2006, Dumitriu, 1996 & Majeti, & Ravi, 2000). Both are polymers of monosaccharide made up of β-(1-4)-2-acetamido-2-deoxy-β-$_D$-glucose and β-(1-4)-2-deoxy-β-D-glucopyranose units, respectively (Figure 2.1).
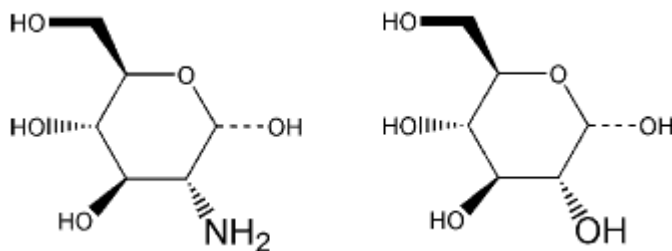

Figure 2.1: Structure of glucosamine (monomer of chitosan) and glucose (monomer of cellulose).

Thus, chitin is poly (β- (1-4) -N-acetyl-d-glucosamine) (Khor, 2001) (Figure. 2.1). In fact, as in the case of cellulose, chitin exists in three different polymorphic forms (α, β and ɣ) (Tong & Yao, 1997). Recent studies have reported that the ɣ form is a variant of α family (Atkins, 1985).
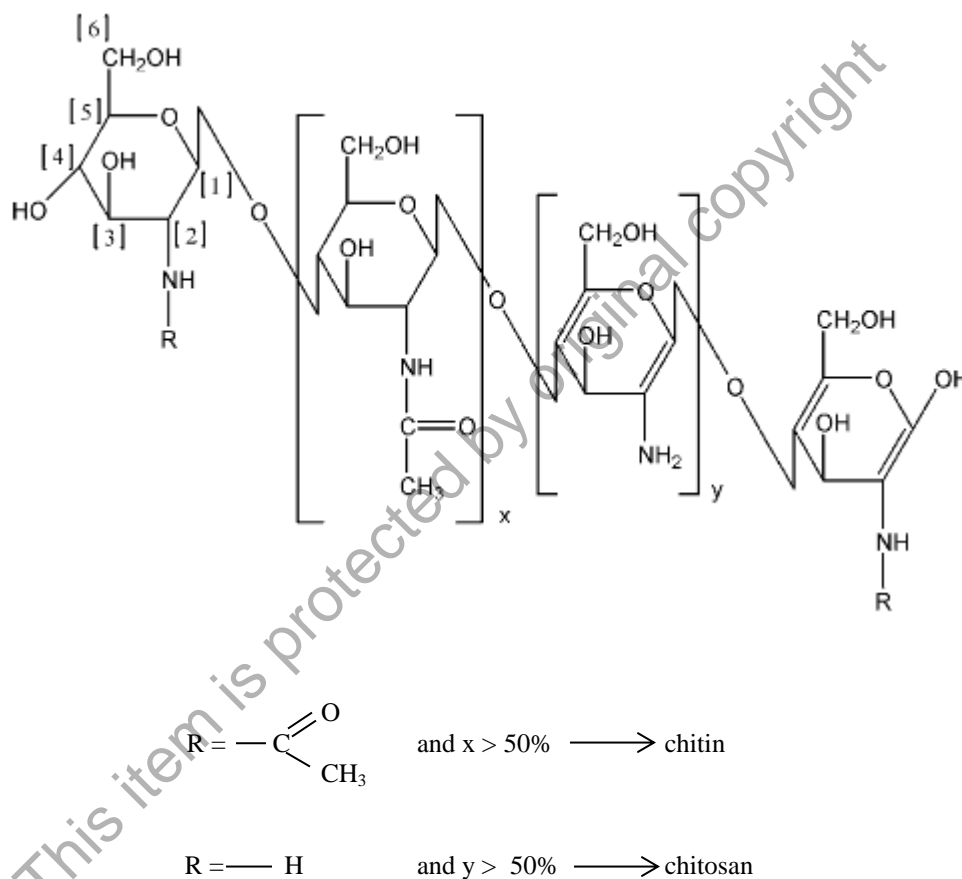

Figure 2.2: Structure of chitin and chitosan (Khor, 2001).

The polymorphic forms of chitin differ in the packing and polarities of adjacent chains in successive sheets; in the β-form, all chains are aligned in a parallel manner, which is not the case in α-chitin. The molecular order of chitin depends on the physiological role and tissue characteristics. The grasping spines of Sagittal are made of pure α-chitin, because they should be suitably hard to hold a prey, while the centric diatom Thalassiosira

contains pure β-chitin. A simple treatment with 20% NaOH followed by washing with water is reported to convert α-chitin to β-chitin (Toffey et al., 1996).

In both structures, the chitin chains are organized in sheets where they are tightly held by a number of intra-sheet hydrogen bonds with the ɣ and β chains packed in antiparallel arrangements (Rinaudo, 2008, Yamaguchi et al., 2005 & Ogawa, 2004). This tight network, dominated by the rather strong C-O-NH hydrogen bonds Figure 2.3, maintains the chains at a distance of about 0.47nm (Minke, 1978). Such a feature is not found in the structure of β-chitin, which is therefore more susceptible than α-chitin to intra-crystalline swelling (Yui et al., 2007).

The current model for the crystalline structure of α-chitin indicates that the inter-sheet hydrogen bonds are distributed in two sets with half occupancy in each set (Minke, 1978). These aspects make evident the insolubility and intractability of chitin (Rinaudo, 2006). In chitin, the degree of acetylation (DA) is typically 0.90 indicating the presence of some amino groups (as some amount of deacetylation might take place during extraction, chitin may also contain about 5-15% amino groups) (Dong et al., 2002). So, the degree of N-acetylation, i.e. the ratio of 2-acetamido-2-deoxy-d-glucopyranose to 2-amino-2-deoxy-d-glucopyranose structural units has a striking effect on chitin solubility and solution properties (Rinaudo, 2006, Dong et al., 2002 & Austin et al., 1981).

Chitosan (CS) is the N-deacetylated derivative of chitin with a typical DA of less than 0.35. It is, thus, a copolymer composed of glucosamine and N-acetylglucosamine. The physical properties of CS depend on a number of parameters such as the molecular weight (from approximately 10,000 to 1 million Dalton), and Degree of deacetylation (DD) in the range of 50-95%, sequence of the amino and the acetamido groups and the purity of the product (Rinaudo, 2008, Austin et al., 1981, & Khor & Lim, 2003). The crustacean shells

(crabs, etc.) which are waste products (now byproducts) of food industry are commercially employed for the production of chitin and CS (Prashanth & Tharanathan, 2007). It is believed that at least 1011 tons (1013 kg) of chitin are synthesized and degraded, but only over 1,50,000 tons of chitin is made available for commercial use.
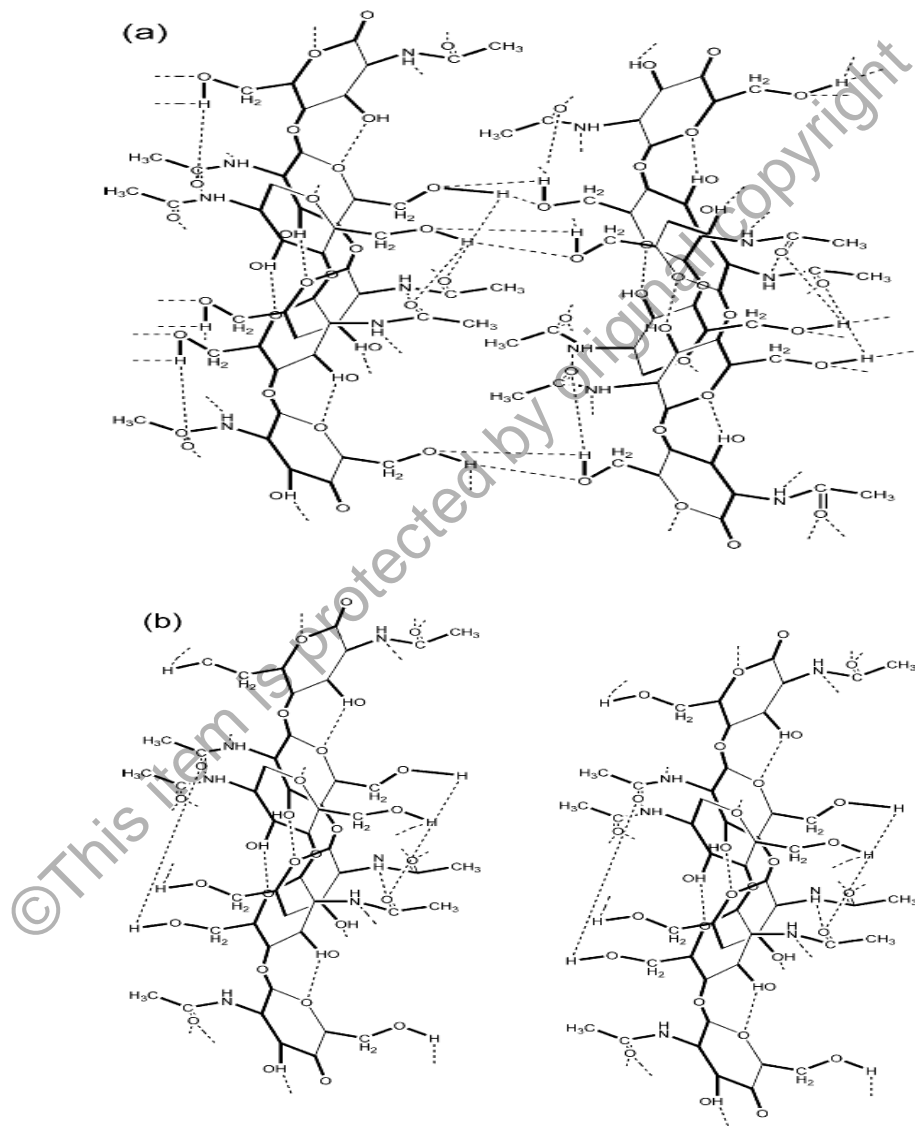

Figure 2.3: Molecular structure and hydrogen bonding in (a) α-chitin and (b) β-chitin (Khor, 2001)

2.1.2   Chemical Modifications

Chitin and CS are interesting polysaccharides because of the presence of the amino functionality, which could be suitably modified to impart desired properties and distinctive biological functions including solubility (Rinaudo, 2006, Hudson & Smith 1998, Tharanathan & Kittur 2003). Apart from the amino groups, they have two hydroxyl functionalities for effecting appropriate chemical modifications to enhance solubility (Dumitriu, 1996). The possible reaction sites for chitin and CS are illustrated in Figure 2.4. As with cellulose (Dumitriu, 1996), chitin and CS can undergo many of the reactions such as etherification (Kurita, 2001 & Gorochovceva & Makusuka, 2004), esterification (Yoshifuji et al., 2006), cross-linking, graft copolymerization (Jayakumar et al., 2005), etc. have summarized the possible chemical modification reactions. A number of authors have reviewed the area emphasizing various aspects of chemical modification of CS (Mourya, 2008, Kurita, 1998, Sashiwa & Aiba, 2004, Jayakumar et al., 2006).
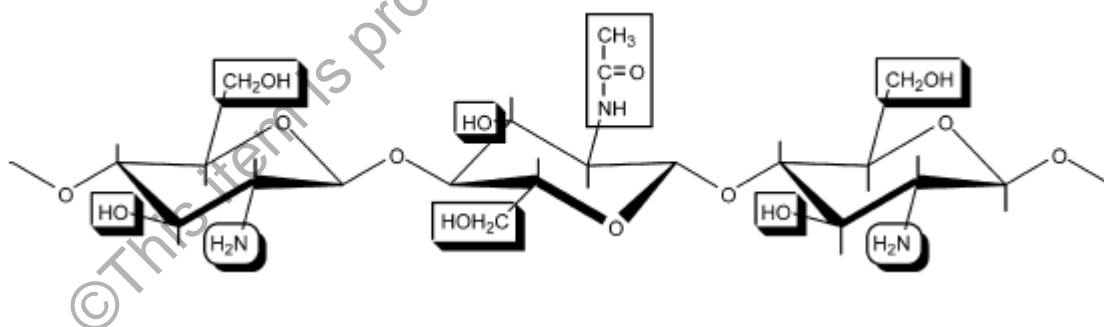

Figure 2.4: Illustration of the possible reaction sites in chitin and chitosan.

The amino functionality gives rise to chemical reactions such as acetylation, quaternization, reactions with aldehydes and ketones (to give Schiff's base) alkylation, grafting, chelation of metals, etc. to provide a variety of products with properties such as antibacterial, anti-fungal, anti-viral, anti-acid, antiulcer, non-toxic, non-allergenic,