Study on Sensing Properties of Chitosan-Polyethylene Oxide-Exfoliated Graphite Based Toluene Sensors

by

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LIST OF ABBREVIATIONS

R&D	Research and Development
CS	Chitosan
PEO	Polyethylene oxide
EG	Exfoliated Graphite
$C_6H_5CH_3$	Methylbenzene
OH	Hydroxyl
COOH	Carboxylic Acid
C=O	Carboxyl
C-C-O	Epoxide Group
NH_2	Amine Group
SEM	Scanning electron microscopy
FTIR	Fourier Transform Infrared Analysis
OH	Hydroxide Ion
O	Oxygen
Chit	Chitin
DVB	Divinylbenzene
H_2O	Water
Ca^{+2}	Calcium ion
$H_2PO_4^{-2}$	Hydrogen Phosphate ion
PEG	Polyethylene glycol
IPN	Interpenetrating Polymer Network
VOC	Volatile Organic Compound

LIST OF SYMBOLS

%	Percentage
Rms	Root Mean Square of Roughness
mA	Mili Volt
mA	Mili Amphere
cm^2	Centimetrecube
rpm	Revolutions Per Minute
^0C	Degree Celsius
Min	Minute
V/K	Volt per Kelvin
V	Volt
Ppb	Part per Billion
Ppm	Part per Million
g	Gram
W/v	Weight per volume
V/v	Volume per volume

Kajian tentang Sifat-Sifat Kitosan-Polietilena Oksida-Grafit Terkapas Berasaskan Pengesan Toluena

ABSTRAK

Kitosan telah digunakan sebagai bahan untuk pembentukan sensor filem kerana struktur dan sifat-sifat di mana ia terdiri daripada kumpulan amino yang mempunyai elektron bebas. Dalam kajian ini, kitosan telah ditambah dengan polietilena oksida dan grafit terkapas untuk mengkaji sifat-sifat elektrik ke arah udara basah dan gas toluena. Serbuk kitosan dilarutkan dalam 2.00 v/v% asid asetik untuk membentuk larutan kitosan. Kemudian, larutan kitosan telah ditambah dengan oksida polietilena dan grafit terkapas berdasarkan nisbah yang diperlukan. Komposisi bahan yang berbeza-beza telah dibentuk diatas papan litar bercetak bersalut emas dengan menggunakan teknik elektrik pemendapan. matriks filem Kitosan/polietilena oksida/grafit terkapas telah disediakan untuk memerhatikan kesan komposisi kandungan grafit terkapas keatas mikrostruktur, kekonduksian elektrik dan sifat-sifat pengesan ketas kitosan. Filem grafit kitosan/polietilena oksida/grafit terkapas telah disediakan dengan pelbagai kepekatan grafit terkapas untuk mendapatkan kepekatan grafit terkapas yang paling sesuai untuk mencapai sifat-sifat elektrik filem yang terbaik. Teknik SEM adalah digunakan untuk menganalisis struktur mikro kitosan/polietilena oksida/grafit terkapas. FTIR telah digunakan untuk menganalisis kewujudan kumpulan fungsian dalam filem yang disediakan kitosan/polietilena oksida/grafit terkapas. Daripada hasil yang diperolehi, projek ini berjaya membuktikan bahawa tambahan 0.4w/v % daripada grafit terkapas ke filem oksida kitosan/polietilena meningkatkan sifat elektrik filem pengesan. Filem kitosan/polietilena oksida/grafit terkapas mempunyai tindak balas, sensitiviti dan kestabilan yang lebih baik berbanding dengan filem oksida kitosan/polietilena.

Study on Sensing Properties of Chitosan/Polyethylene Oxide/Exfoliated Graphite Based Toluene Sensor

ABSTRACT

Chitosan was used as a material to fabricate film sensor because of its structure and properties where it consists of amino group which has free electron. In this study, chitosan was added with polyethylene oxide and exfoliated graphite to study the electrical properties toward wet air, dry air and toluene. Chitosan powder was dissolved in 2.00 v/v% of acetic acid to form chitosan solution. Then, the chitosan solution was added with polyethylene oxide and exfoliated graphite based on the ratio needed. The composition of the materials was varied and fabricated on gold plated printed circuit board by using electrical deposition technique. Chitosan/polyethylene oxide/exfoliated graphite matrix films were prepared to observe the effect of exfoliated graphite concentration on microstructure, electrical conductivity, and sensing properties of the films. The chitosan/polyethylene oxide/exfoliated graphite film was prepared with various concentration of exfoliated graphite to obtain the best concentration of exfoliated graphite to achieve the excellent properties of the films. The SEM technique was employed to analyse the micro- structure of the prepared chitosan/ polyethylene oxide / exfoliated graphite. The FT-IR was used to analyse the functional groups existence in the chitosan/polyethylene oxide/exfoliated graphite films. From the result obtained, this project successfully proved that the addition 0.4w/v % of exfoliated graphite onto chitosan/polyethylene oxide film has improved the sensing properties of the films. The chitosan/polyethylene oxide/exfoliated graphite films have better response, sensitivity and stability compare to chitosan/polyethylene oxide films.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The worldwide research and development (R&D), the sensors have been expanded in the number of active research, published literature and economic investment, since 20 years ago. The sensor is used to give information about chemical, physical and biological environment. Sensor to a tool that sense temperature, pressure, flow rate, pH, radio waves or sound that can change into a functional input signal with the unlimited value or adjust in a physical quantity (Saloman et al., 2010). Also in early 1947, the studies of electronic properties of the graphite trough tight-binding method and the concept of the graphene were intended by (Wallace). He was described that graphite has a small amount of valence bond elongated to the conduction band and concluded that graphite is semi-conductive material without activation energy. Graphene is a two dimensional crystal and a one-atom-thick that was determined as primary building block for major sp^2 graphitic material in graphite, carbon nanotubes and fullerenes. Regarding to the unique structure, graphene required the special properties distinct with carbon materials such as remarkable electrical properties of electron transferring competes (Song et al., 2014).

Chitosan is a linear, semi-crystalline polysaccharide composed of (1→4)-2-acetamido-2-deoxy-b-D-glucan (N-acetyl D-glucosamine) and (1→4)-2-amino-2-deoxyb- D-glucan (D-glucosamine) units (Rinaudo et al., 2006). As such, chitosan is not extensively present in the environment – however, it can be easily derived from the partial deacetylation of a natural polymer. Chitosan is a polycationic polymer that contains of one amino group and two hydroxyl groups in the repeating glucosidic excess. Furthermore, chitosan has rigid crystalline structure over intra and inter-molecular bonding of hydrogen. In general, chitosan was obtained from de acetylation of chitin whereby it found in the skeleton of insects, crustacean and some fungi. The shell waste of crabs, lobsters, krills and shrimps is the main commercial sources of chitin. The every year, there are several millions ton of chitin are harvested and thus it represent a cheap and readily available source (Dash et al., 2011).

The chitosan is cationic polyelectrolyte and the membrane of chitosan also used active transport of chloride ions in aqueous solution. Chitosan film has a very low electrical conductivity. Nevertheless, when a chitosan membrane is expanded in water, its amino groups may be protonated and hence donates to ionic conduction in the membrane. Highly crystalline parts in the chitosan membranes certainly present resistance to water uptake and in turn hinder hydroxide ion transport in the membrane due to crystalline nature of chitosan. To increase the ionic conductivity of the membrane in expanded or swollen state, the chemical modification can be applied to enlarge the hydrophilicity of the membrane and decrease crystallinity of the membrane.

Chitosan is widely as a sensing material due to its capable to be selectivity deposited and largely contained of amino acid group in their chains. So the chitosan composed of high amino acid group, there will produce an active bonding chain and sustained to maintain its natural properties despite treated into film. The fabrication of chitosan film on electrodes surface was attracted human to develop the novel sensor (Dash et al., 2011). Fabrication of the sensor was followed by annealing process and electrical testing. The sensor fabrication must have good sensing properties such as response time, recovery, excellent in sensitivity, stability, repeatability, reproducibility and recovery.

It has been proved that the chitosan based sensor have a good performance in detecting the presences of gas sensor. The chitosan sensor produces a good response and has an absolute and quick recovery. So, the response or initial time to the sensor to detect the presence of molecule on chitosan film sensor close to 10 sec for every concentration which is indicates the fast detection the sensor (Dash et al., 2011). Toluene is also used as drug for its intoxicating properties. However, inhaling toluene has potential to cause severe neurological harm. Toxicity can occur from unintentional or deliberate inhalation of fumes, ingestion, or transdermal absorption. Also it dangerous and can give effect to human skin, nervous system and mucous membrane. Toluene used as varnishes, lacquers, in adhesive and others. Among these at room temperature the chacterstic of toluene is bad smell, toxic gas and can be revealing by solid state gas sensor. Many exposure are able to influence the nervous system during breath and cause dizziness, confusion, headaches and able to lead to death. The people which breathe large amounts of toluene undergo a loss of hearing, memory loss, tremors and other symptoms. This substance as well influences a person health throughout contact with the skin.

Before any further developed in the sensor application, a laboratory scaled experimental must first be conducted to determine the nature of chitosan based film towards electrical response. In the previous study, chitosan powder was dissolved in 2% of acetic acid to obtain a solution gel. The solution would be then deposited onto a gold plated printed circuit board (PCB) via electro-deposition method.

In this research, chitosan was chosen to be further developed by incorporating it with polyethylene oxide (PEO) and exfoliated graphite (EG). The electrical study was conducted based on the requirement to produce a biosensor with high selectivity and lifetime. The blend of chitosan/polyethylene oxide/exfoliated graphite was prepared with various the ratio of exfoliated graphite (EG). In the system, EG serves as a conductive filler to provide a better sensitivity in electrical response. The sample should be focused on the electrical testing to detect wet air and dry air content before exposing it to toluene gas as an analyate.

As current flows, it causes the positive plate be positively charged whilst the negative plate to be negatively charged. Electro deposition manifests the pH where chitosan is most soluble that occur in the areas of high pH. When more hydrogen evaluates, pH would gradually increase (Jagiello et al., 2014). The current density can be controlled which in this study, a voltage of 2.5 V deposition voltage is used to fabricate chitosan sensor.

The metal-oxide based semi-conductor gave an extremely high sensitivity to many types of gases however providing low selectivity as such overlapping of conductance and valence band a response that are hard to distinguish from analyte to another. Generally toluene can be measured in blood and urine but however the detection of toluene cannot predict the kind of health effects that might generate from the exposure. Toluene can harm people through several factors such as the quantity of the duration and how long you happen to face it. When human breath toluene it is taken straightly into human blood from lungs and it is similar when human touch materials containing toluene or bath in water containing toluene, so the toluene can pass through human skin into bloodstream.

1.2 Problem Statements

Chitosan is a weak conductivity film and has low electrical properties and is not really good thermal stability. To improve electrical properties of chitosan, so the exfoliated graphite was added as conductive filler. It was believed that addition of the material can enhance the electrical properties of the chitosan. Exfoliated graphite also is a cheaper material compared to graphene oxide materials. It can improve the sensing properties. Furthermore, the chitosan has poor dispersion properties. Addition of exfoliated graphite can enhance the interaction between exfoliated graphite and matrix since exfoliated graphite has good dispersion properties. Additionally, exfoliated graphite blending with chitosan formed a new mixture as epoxy group of that will interact with primary amine group in chitosan. Thus, it can enhance the reaction between polyethylene oxide and chitosan. Besides, the addition of polyethylene oxide in chitosan can improve the electrical properties of chitosan well because polyethylene oxide the ability to solvate ionic salts and forms solid polymer electrolyte.

Exposure to toluene can affect different people in different ways. High exposure of toluene might lead to life threatening issue for human. It is important to monitor the toluene exposure in certain industry. It is very dangerous activity if human exposed to high level of toluene in a short time with purposely inhaling or sniffing glue or paint. Moreover, there are high possibility to damage the human kidneys and liver when expose to large amount of toluene.

1.3 Objectives of the Study

The main objectives of this research are:

1. To study the effect of polyethylene oxide (PEO) on morphology and electrical properties of chitosan film.
2. To study the effect of exfoliated graphite (EG) on morphology and electrical properties of chitosan/polyethylene oxide films.
3. To study the sensing properties of chitosan/polyethylene oxide/exfoliated graphite films toward toluene.

1.4 Scope of Study

This study is focused on the preparation of sample in accordance to various designed formulation. Chitosan solution was first prepared as a gel by mixing with acetic acid solution then polyethylene oxide solution was prepared by mixing with acetic acid. Next, the pure chitosan is tested with the dry air and wet air to obtain a pure chitosan electrical response in term recovery, repeatability and its sensitivity, and response time. Then the gel of chitosan was mixed into polyethylene oxide to produce CS/PEO solution until dilute homogeneous.

Exfoliated graphite was then added into the chitosan/polyethylene oxide blend. The study concerns the electrical properties by addition of exfoliated graphite which at the same time was expected to gives better dispersion within film sensor. Testing includes the voltage response generated when exposed to dry air wet air and toluene. The response was observed throughout the concentration of chitosan/polyethylene oxide and exfoliated graphite content.

The composition differences between exfoliated graphite and chitosan in this study are obvious in order to study effect different concentration of exfoliated graphite towards the thermal and electrical properties of CS/PEO/EG films. Sensing properties of CS/PEO/EG films sensor toward toluene is also study by observing the response of the sensor term of detecting toluene vapor. The forming of the gas or vapor sensor indicates the important characteristics such as sensitivity, good reproducibility, selectivity, recovery time and fast response time.

In addition, for characterization of CS/PEO/EG films some testing such as Fourier transform infrared spectrometry (FT-IR) and scanning electron microscopic (SEM) were done.

CHAPTER 2

LITERATURE REVIEW

2.1 Chitosan

Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating shrimp and other crustacean shells with the alkali, sodium hydroxide. Chitosan has a number of commercial and possible biomedical uses. It can be used in agriculture as a seed treatment and bio pesticide, helping plants to fight off fungal infections. In winemaking it can be used as a fining agent, also helping to prevent spoilage. In industry, it can be used in a self-healing polyurethane paint coating. In medicine, it may be useful in bandages to reduce bleeding and as an antibacterial agent; it can also be used to help deliver drugs through the skin. More controversially, chitosan has been asserted to have use in limiting fat absorption, which would make it useful for dieting, but there is evidence against this. Other uses of chitosan that have been researched include use as a soluble dietary fiber.

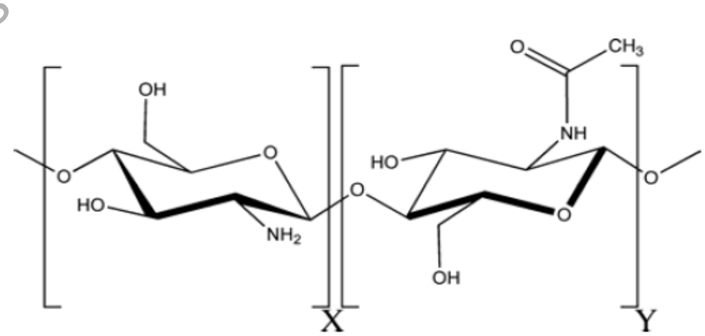

Figure 2.1: Structure of chitosan composed of β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit).

Figure 2.1 shows the general structure of chitosan. It has amine group attached at the second carbon that contributes too much of its chemical behavior. Apart from that, other functional groups in presence are two hydroxyl groups attached at third and last carbon. Chitosan is a biomaterial, primarily produced from the alkaline deacetylation (40–50% NaOH) of chitin where this N-deacetylation is almost never complete. The chitosan is considered as a partially N-deacetylated derivative of chitin. It is an abundant natural biopolymer obtained from the exoskeletons of crustaceans and arthropods which is a non-toxic copolymer consisting of b-(1,4)-2-acetamido-2-deoxy-D-glucose and b-(1,4)-2-anaino-2-deoxy-D-glucose units. Each glucosamine unit contains a free amino group, and these groups can take on a positive charge which gives amazing properties of chitosan, it's useful in a wide application in various industries such as pharmaceuticals, biochemistry, biotechnology, cosmetic, biomedical, paper industry, food and textile industries and others (Muzzarelli, 1997). These biopolymers offer a wide range of unique applications including bioconversion for the production of value-added (Shahidi & Jeon et al., 1999).

Respectively, there are three types of functional group in chitosan which is amino group and both secondary hydroxyl groups at the carbon 2, carbon 3, and carbon 6 site. Chitosan is attractive material due to its properties comprising its good adhesion, biocompatibility, non-toxicity, and excellent film forming capability. Chitosan hydrogel could be chemically deposited toward electrodes as well it can firmly connected to the electrode and maintain their original properties (Du & Zhang et al., 2007).

Chitosan generally used to prepare films, hydrogels and fibers and materials mostly used in biomedical application for which biocompatibility are important. The stability of chitosan materials is ordinarily lower due to their more hydrophilic properties and primarily its pH sensitivity. Therefore the chitosan is easier to process than chitin (Rinaudo et al., 2006). Chitosan has a wide range in biomedical application and hydroxyl and amino group in the structure can serves as donors (Buraidah & Arof et al., 2011).

2.2 Chitosan Properties

Chitosan is categorized in the highly basic polysaccharides and commonly known as a biocompatible in animal tissues, odorless, enzymatically biodegradable, and non-toxic. Chitosan are able to chelation with metal ions, form films, polyoxysalt formation and optical structural properties. The characteristics of chitosan is depends on the degree of deacetylation and its molecular weight which is affect the rheological, physical properties and solubility. Chitosan familiar as a semi-crystalline material and the molecular weight of chitosan products is depend on the increasing of deacetylation which is defined as the degree of crystallinity. The removal of acetyl groups from the molecular chain of chitin, leaving behind a complete amino group (-NH_2) is known as the process of deacetylation. By using the viscometric method, the molecular weight of chitosan can be determined (Martinez-Camacho & Castillo-Ortega et al., 2010). Chitosan is generally polydispersed and able to disperse in definite organic and inorganic acids like lactic acid, hydrochloric acid, succinic acid, phosphoric acid, acetic acid, propionic acid, citric acid and formic acid after prolonged stirring at specific pH values. It was reported that white gelatinous precipitate produced after dissolution when nitric acid is used to dissolve chitosan. However, chitosan cannot be dissolve by sulphuric acid since there will create a reaction to produce chitosan sulphate namely a white crystalline solid (Cheen, 2008). The chitosan solubility is affected by concentration and acids pka value.

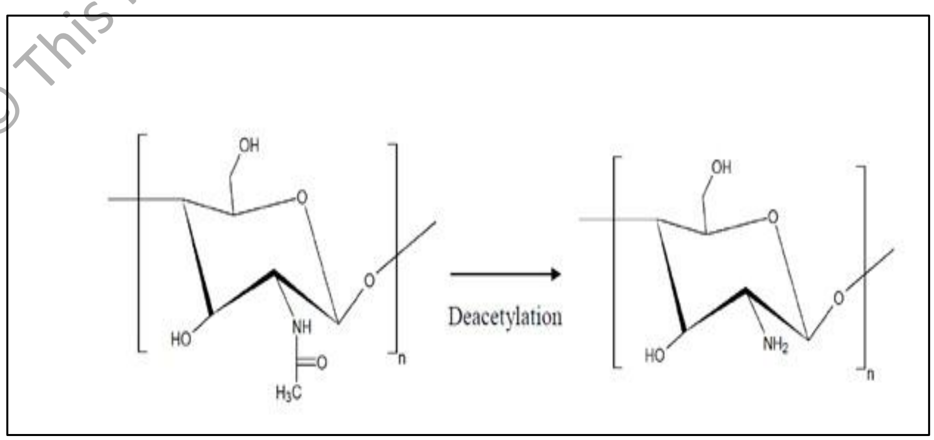

Figure 2.2: Deacetylation of chitin to chitosan.

Figure 2.2 shows deacetylation of chitosan can be described as the removal process of acetyl group from chitin. In comparison to both of the structure, chitin and chitosan very similar except that the degree of acetylation is differing by each other 50% as chitosan. Roughly, DA>50% are called chitin while any less than that is characterized product to another id differs as it is dependent on the crustacean species used as well the method of preparation. So the big numerous of amino groups in chitosan sequence it could be simply protonated through acrylic acid and can caused slightly poly-base of chitosan. The positive charge incited the electrostatic opposition between the bind of chitosan, it could affected loose the chain partition (Nguyen & Liu et al., 2013). Chitosan is readily soluble in diluted acidic aqueous solutions and easily processed. Nevertheless, chitin is insoluble in most solvents and difficult to process into useful materials. Moreover, chitosan show unique physicochemical properties like biocompatibility, antimicrobial activity, biodegradability and excellent film-forming ability. The properties of chitosan such as insoluble in water, aqueous alkaline solutions and common organic solvents enable chitosan used in many application although it was readily soluble in aqueous inorganic and organic acid media. Addition, chitosan is degraded by enzymatic hydrolysis but its tensile strength and elasticity is not available for a few applications of biomedical such as skin tissue replacement and wound dressing (Cheaburu & Vasil et al., 2012). Chitosan in general is biopolymer with high molecular weight. Chitin alone would usually have molecular weight more than 1,000,000 Dalton. It is classified as chitosan when more than 50% chitin is deacetylated. (Wenham et al., 2013). Commercial chitosan would usually range from 100,000 – 1,200,000 Daltons (Rathore & Sharma et al., 2008). It must be taken note however that the molecular weight would decrease upon an increase in temperature. Beyond temperature 280C^{o} for instance, would cause a thermal degradation where chain slippage and further broken down into smaller parts. Chitosan has a semi crystalline structure in its solid state but are soluble in aqueous solutions. It is soluble when the amine group at the second carbon repeat unit is protonated while the rest of the polysaccharide turns into polyelectrolyte in acidic medium. Commonly, only one percent of acetic acid or 0.1M of acetic acid is required to test the solubility of chitosan. The amounts of proton required are of at least the same amount from the amount of amine unit present. Chitosan, being a linear polysaccharide, has many advantageous properties that can be harvested as a potential biomaterial in s medical application.

2.3 Chitin Properties

Its parent structure chitin is a long chain homopolymer**.** The many carriers that have been considered and studied for organic or inorganic, natural or synthetic, chitin and chitosan are of interest in that they offer most of the above characteristics. Chitin and chitosan are natural polyaminosaccharides, chitin being one of the world's most plentiful, renewable organic resources. A major constituent of the shells of crustaceans, the exoskeletons of insects and the cell walls of fungi where it provides strength and stability, chitin is estimated to be synthesized and degraded in the biosphere in the vast amount of at least 10 get each year. Chemically, chitin is composed of β (1 → 4) linked 2-acetamido-2-deoxy-β-d-glucose units (or *N*-acetyl-d-glucosamine), forming a long chain linear polymer. It is insoluble in most solvents (Davis, 2011).

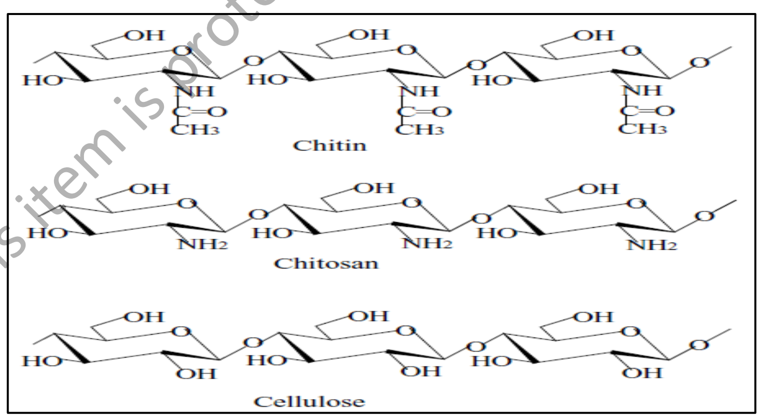

Figure 2.3: Structure of Chitin, Chitosan and Cellulose

Figure 2.3: shows the chitin formula Chitin ($C_8H_{13}O_5N$)n is mainly found in nvertebrates in animal reign. Cellulose formula ($C_6H_{10}O_5$)n is a major compound of cell walls of plants.