Milk powder quality degradation detection using chitosan film based sensor

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Abstract. Chitosan based milk powder quality degradation sensors have been successfully fabricated by combining electrochemical deposition and photolithography techniques. The aim of this paper is to discuss the potential of chitosan thin film sensors for detecting milk powder quality degradation. The milk powder quality may be decreased upon storage. Milk powder surface composition changes during storage due to increasing in moisture content. Electrical testing of chitosan thin film properties to fresh milk powder and milk powder exposed to air for 1, 2, 3 and 4 weeks has been done at room temperature. The results show that the chitosan-based milk powder quality degradation sensors have good performance demonstrated by very good response, stability, recovery, repeatability and selectivity. The simple, easy and inexpensive technique is required to monitor the milk powder quality degradation.

1. Introduction
Milk powder is one of the most important foodstuffs which produced in large scale [1]. Milk powders are widely used in food-processing industries, such as manufacture of chocolate, bakeries and ice cream factories. However, its quality may be decreased upon storage [2]. The surface composition of milk powders can be changed during storage and it may deteriorate many powder properties that exist in between particles and environments (e.g. wettability, oxidative stability and flow ability.) [3]. Milk quality is affected by microbial spoilage due to undesirable off odours, physical defects and secondary metabolite toxicity [4]. Other than that, milk may undergo oxidation process when it is exposed to air. The oxidation process will release volatile gas such as hexanal, heptanal and heptanone [5].

Conventional analytical method used to detect the volatile compound is gas chromatography/mass spectrometry (GC-MS) [4]. However, the equipment cannot be used for in-situ detecting milk quality degradation due to its large size, heavy, high cost and time consume operation. In addition, the equipment also needs to be handled by skilful operator in order to have accurate result. Therefore, simple, easy and inexpensive method is required to monitor the degradation of milk quality.
Conducting polymers such as polyaniline and polypyrrole have received a great attention as chemical, biological, and gas sensors [6-11]. Polymer based sensors can operate at room temperature compared to semiconductor-based sensors so it can eliminate the requirement for high power consumption. This is one of the main reasons for the intensive investigation and development of these materials [12]. In this study, chitosan was chosen as a sensing material for milk powder quality degradation sensor fabrication.

Chitosan is a biopolymer that is suited for biological micro-devices due to its ability to be selectivity deposited and its high density of amine groups which provide active bonding site [13]. Chitosan is a natural reproducible polymer which has good film forming properties and low cost [14]. Chitosan can be electrochemically deposited on to a metal plate to fabricate film sensors. To date, there is no report on the utilization of chitosan as a sensing material for milk powder quality degradation detection.

The sensor characterizations have been done using scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The electrical characteristics of chitosan-based milk powder quality degradation sensors were carried out by exposing air which flow through milk powder to the surface of the chitosan thin film sensors. The sensing properties of chitosan film, i.e. response, stability, recovery, repeatability and selectivity have been tested by measuring the output voltage when the chitosan film was exposed to fresh milk powder and milk powder exposed to air for 1 week, 2 weeks, 3 weeks and 4 weeks.

2. Experimental

Chitosan powder (medium grade, 99.9% purity) and acetic acid were purchased from Sigma Aldrich Ltd. The 2% chitosan solution gel was prepared by dissolving chitosan powder in 2% acetic acid and stirred using a magnetic bar for 24 hours at room temperature. The rotation speed is 500 rpm. The chitosan thin film sensors were fabricated by combining photolithography technique and electrochemical deposition technique as described in our previous report [15]. A piece of patterned aluminium was dipped into chitosan solution gel using an electrochemical deposition technique. Milk powder which has been used in this study is Nestle milk powder with brand “Everyday”.

The electrical testing was carried out using the experimental setup as illustrated in our previous report [15], in which each milk powder with different condition was placed into a sealed small container. The sensor was exposed to both fresh milk powder and milk powder exposed to air for 1, 2, 3 and 4 weeks. The exposure was done by flow the air through the milk powder container to bring along the molecules released by milk powder onto the sensor surface. The readings were taken for every 30 seconds exposure, where the exposure was repeated five times continuously. The data was plotted into the graphs and then the graphs were interpreted to explain the electrical properties of chitosan sensor in detecting the milk powder quality degradation. The properties include response, stability, recovery, repeatability and selectivity.

FT-IR spectra measurements were conducted using a Perkin Elmer RX1 FT-IR spectrometer. The surface morphology of chitosan was examined by using a Jeol JSM- 6460LA scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. The results of characterization were related to the electrical properties of chitosan film sensor to show the relation between morphology of chitosan film and performance of chitosan film sensors in detecting milk powder quality degradation. Moisture content measurement was conducted using Sartorius MA35 moisture content analyser. The measurement aims to know the moisture content of milk powder after exposed to air for 1, 2, 3 and 4 weeks.

3. Results and Discussion

The FTIR spectra of the chitosan film are shown in Fig. 1. In the spectrum of chitosan, the absorption peaks at 3247 cm\(^{-1}\) and 2920.0 cm\(^{-1}\) are due to overlapping of NH\(_2\) and OH [14, 16-17]. The band occurring at 2339.99 cm\(^{-1}\) and 2359.90 cm\(^{-1}\) are ascribed to the O-H stretching mode in chitosan indicating existing of acid group. The absorption band at 1637.94 cm\(^{-1}\) is due the C=O group [14]. The
absorption band at 1551.34 cm\(^{-1}\) is ascribed to the N-H band. The absorption peak at 1407.79 cm\(^{-1}\) indicates the existence of OH group [17]. There are C-N group attribute to the amino group at absorption peak of 1333.49 cm\(^{-1}\) and 1325.96 cm\(^{-1}\) [14]. The absorption peaks at 1149.04 cm\(^{-1}\), 1044.44 cm\(^{-1}\), 1064.69 cm\(^{-1}\) and 1020.09 cm\(^{-1}\) indicate the existence of C-O group [17].

**Figure 1.** Infrared spectra of chitosan film

**Fig. 2** illustrates the FT-IR spectra of fresh milk powder and milk powder which was exposed to air for 1 week, 2 weeks, 3 weeks and 4 weeks. Protein content in the milk powder was characterized by presence of amide I, amide II, and amide III bands near 1650 cm\(^{-1}\), 1550 cm\(^{-1}\), and 1450 cm\(^{-1}\), respectively. In addition, the presence of amide can be confirmed by the N-H stretching band near 3350 cm\(^{-1}\). The presence of the glucose can be determined from C=O of aldehyde at 1740 cm\(^{-1}\) – 1720 cm\(^{-1}\) bands. On the other hand, carbohydrate can be determined by presence of broad C-O bands near 1080 cm\(^{-1}\) and O-H group at 3300 cm\(^{-1}\) [17]. It is clearly can be seen that O-H group at 3300 cm\(^{-1}\) broaden. There are O-H stretching group in region of 2339.99 cm\(^{-1}\) and 2359.90 cm\(^{-1}\) indicating existing of acid group. The FT-IR spectrum shows a broad change in the region of 3350 cm\(^{-1}\). This is due to the Maillard reaction within the milk powder where amino acid from protein underwent reaction with the carbohydrate [18]. The broaden band at 1080 cm\(^{-1}\) can be seen in this spectrum which indicates the carbohydrate underwent reaction [18]. The reason for these phenomena is water molecules absorption and oxidation process which occurred during milk powder exposed to the air.
Figure 2. FT-IR spectra of fresh milk powder and milk powder exposed to air for 1 week, 2 weeks, 3 weeks and 4 weeks.

Figure 3. SEM micrograph of chitosan thin film

The SEM micrograph of chitosan film is represented as in Fig. 3. The surface of chitosan thin film sensor is smooth indicating that the chitosan solution gel was well deposited on aluminium substrate to form a uniform layer of film. The smooth surface makes the chitosan film layer adheres strongly onto the aluminium surface and enhance the electrical properties of the chitosan film. However, it can be seen that there are some small cavities formed on the surface of the chitosan film which was caused by formation of bubbles on the chitosan film layer during electrochemical deposition process. The present of small cavities is believed can aid for absorbing the water molecules and gas which are released from milk powder. Therefor the water molecules and gas flow through the chitosan body to give different respond [15].
Fig. 4 shows the response of chitosan-based milk powder quality degradation sensor exposed to fresh milk powder and milk powder exposed to air for 1 week, 2 weeks and 4 weeks as well as the changes in operating temperature and humidity during testing. The sensor response values are calculated as the ratio \((R_{\text{milk}} - R_{\text{air}}) / R_{\text{air}} \times 100\%\) where \(R_{\text{milk}}\) and \(R_{\text{air}}\) are the electrical resistance values of sensor in milk and normal air, respectively. The chitosan-based milk powder quality degradation sensor shows good response to fresh milk powder and milk powder exposed to air for 1 week until 4 weeks. Fig. 4 describes the exposure of the sensor to milk powder, at supplied voltage under 1.5 V, the chitosan-based milk powder quality degradation sensors yield response values of approximately 25, 36, 45, 57 and 58\% when they are exposed to fresh milk powder and milk powder exposed to air for 1 week, 2 weeks, 3 weeks and 4 weeks respectively. However, the sensor became saturated when it was exposed to milk powder exposed to air for 4 weeks, the sensor did not show increasing in response. The saturation indicates that the limit of sensor’s ability to detect the degradation of milk powder quality is until 4\textsuperscript{th} week exposure to air. During the electrical testing, chitosan thin film sensor obeyed the other sensing properties which include good stability, complete recovery, good repeatability and good selectivity.

![Graph showing electrical response of chitosan based milk powder quality degradation sensor](image)

**Figure 4.** The electrical response of chitosan based milk powder quality degradation sensor

Milk powder surface composition changes during storage due to increasing in moisture content. It was proved by FT-IR spectrum of milk powder exposed to air for 1 until 4 weeks. The FT-IR spectrums of milk powder exposed to air for 1 week until 4 weeks broaden especially O-H bands. Some studies reported that the amount of volatile gas produced increases proportionally with the storage time of milk [5, 19]. Chitosan is a unique material which consists of NH\(_2\), an amino group with a lone pair of electrons; as such, its nucleophilicity is very strong [20]. The lone pair electrons play important role in electrical properties of the chitosan sensor. Therefore, the amine is capable to interact with water molecules and volatile gas.

The mechanism of sensing properties of sensor starts when oxygen in air takes electron from the surface of chitosan and becomes chemical absorbed oxygen \((O^-, O^+, O_{2^-})\) as explained in equation (1-4) [19]. The chemisorbed oxygen forms electron potential barrier and hence, it decreases the conductivity of chitosan or increases its resistance. When this happens, it will be hard for electrons to jump from valance band to conduction band.
As can be seen in Fig. 4, when the chitosan thin film sensor was exposed to milk powder, the electrical responses increase proportionally with the milk powder exposure time. The longer exposure time, the electrical response of the sensor is higher. There are two reasons why these phenomena occurred. First, the milk powders, both fresh and milk powder exposed to air, have different moisture content. Chitosan has been well known that the chitosan is sensitive to water molecules [21]. Water molecules which are absorbed by milk powder interacted with the chemisorbed oxygen which occupies the surface of chitosan film to release the trapped electrons, hence the electrical response rose. The detail explanation about interaction of chitosan and water molecules was reported in our previous report [15]. This case was supported by FTIR results in Fig. 2 where the O-H group of milk molecules broaden as the exposure time of milk powder increases and it was proved as well by the data of moisture content in Fig. 5. Fig. 5 shows the moisture content of the milk powder with different condition. The figure can be used to explain why response values increased when the sensors was exposed to milk powder. From Fig. 5, it can be seen that the fresh milk powder itself consists of moisture. The moisture content of fresh milk powder is 2.92%. This is why the sensor gave response when it was exposed to fresh milk powder. The moisture content increased up to 4.34% and 7.11% when it was exposed to air for 1 week and 2 weeks. The moisture content seems to become saturate in week 3 and 4, the moisture content for week 3 and 4 are 7.99% and 8.18%. These results are appropriate with the response values given by the sensor where the response values of milk powder exposed to air for 3 weeks and 4 weeks give almost similar reading.

![Figure 5. Moisture content of milk powder](image)

The second reason is due to the milk which tends to produce some volatile gases when it is exposed to air because of oxidation process occurs when milk is exposed to air. The oxidation process will release volatile gases such as hexanal and heptanal [5]. Based on the previous study reported by Jing Wang [23], when the chemisorbed oxygen meets volatile gas such as formaldehyde, the gas molecules react with the chemisorbed oxygen to release electron which contributes to increase in response.

This reaction may occur in this case since aldehyde gas such as hexanal or heptanal released upon oxidation process for most of the dairy products [5, 22]. During reaction of chitosan and aldehyde gas, the density of chemisorbed oxygen decreases and the potential barrier becomes lower, and in turns, the free electrons flow easier. Hence, the electrical response of the chitosan film sensor increases. However, in the case of milk powder, the first reason why the electrical response values increase when the milk powder exposure upon the surface of chitosan film is seem to be more reasonable because it
has been proved by data of moisture content measurement and FT-IR spectrums of milk powder after exposed to air for 1 until 4 weeks.

4. Conclusion
The chitosan-based milk powder quality degradation sensor has been successfully fabricated. The chitosan- based milk powder quality degradation sensor can operate well and electrical testing showed that this sensor has good performance which demonstrated by good response, stable, good recovery, excellent repeatability and good selectivity. The response of the sensor when it was exposed to air is higher compared to fresh milk powder. Therefore, the chitosan thin film sensor has a big potential for detecting milk powder quality degradation.

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