Improved Electrical Properties of Chitosan Based Acetone Sensor by Adding Carboxymethylcellulose (CMC)

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Abstract. The acetone sensors based on chitosan have been successfully fabricated using an electrochemical deposition method. The physical and electrical characterizations of chitosan film were carried out to observe the performance of the sensor. The results showed that the chitosan based acetone sensors exhibited fast response, complete recovery and good stability. However, the improvement of chitosan films is still necessary due to the poor surface, low repeatability and reproducibility. Therefore, the objective of this study is to modify chitosan film performance by adding CMC into chitosan solution with the variation of 0.01, 0.05, 0.1 and 0.5 g. The characterization of chitosan and chitosan-CMC films were investigated using PSA, optic microscope, DTA and FTIR. While the electrical properties were observed by exposing the sensors to acetone gas for various concentrations. The results showed that acetone sensor based on chitosan-0.05 w/v CMC has the best physical and electrical properties such as homogeneous surface, high thermal property, fast response, complete recovery, good repeatability and excellent reproducibility. Thus, the addition of CMC can improve the performance of chitosan based acetone sensors.

1. Introduction

Chitosan is high molecular weight linear cationic polysaccharide obtained by extensive deacetylation of chitin which is widely distributed in the exoskeleton crustaceans and the second most abundant natural biopolymer after cellulose [1-6]. Due to its attractive properties including biodegradability, biocompatibility, non-toxicity, electrolytic, adsorbability, chemical-resistance and film forming [7-14], chitosan has attracted a great interest as a biomaterial for various applications such as biomedical [15,16], food package [17], pharmaceutical [18], wound dressing material [19], and issue engineering [20]. Furthermore, chitosan has high density of amine groups which provide active bonding sites [21] and it has the ability to retain its natural properties even after being processed into film [22]. Thus, chitosan was selected to be used as sensing material by fabricating into film form using electrochemical deposition method.
However, weak mechanical strength and low electrical conductivity of chitosan has limited their further applications [23, 24]. Moreover, films fabricated from pure chitosan tend to be rigid and brittle. Therefore, several approaches have been proposed to improve these undesired properties of chitosan by adding other polymer as additives which are plasticizer in the preparation of chitosan films. The addition of plasticizer is expected to improve these undesired properties [25]. CMC is one of the types of plasticizers that can be used due to it is a natural biodegradable, nontoxic and biocompatible anionic polymer gained from natural cellulose by chemical modification [26-30]. CMC is relatively similar to chitosan in structure where they have strong ionic bond that allows CMC to improve the characteristics of chitosan film [31]. Therefore, the objective of this study is to modify chitosan film performance by adding CMC into chitosan solution with the variation of 0.01, 0.05, 0.1 and 0.5 g and fabricated using an electrochemical deposition technique. The characterization of chitosan and chitosan-CMC films were investigated using PSA, optic microscope, DTA and FTIR. While the electrical properties were observed by exposing the sensors to acetone gas for various concentrations.

2. Experimental

2.1. Material
Chitosan powder (Sigma Aldrich, pro analytical grade) produced by treating seafood waste was used as a sensor material. Acetic acid (Glacial) obtained from Merck Millipore was selected as a solvent while CMC (Aqualon) was used as an additive.

2.2. Sensor Fabrication

2.2.1. Solution preparation. Chitosan and chitosan-CMC solutions were prepared by dissolving chitosan and CMC powder in 2% acetic acid using magnetic stirrer with the rotation speed of 300 rpm for 24 h at room temperature. The mass variation of CMC is 0.01, 0.05, 0.1 and 0.5 g.

2.2.2. Gold Layer Patterning. Epoxy was used as a substrate and gold layer was coated onto the epoxy substrate surface. Then, gold layer was patterned by a printing method. The epoxy substrate was cut in size 0.5 mm.

2.2.3. Film Preparation. The chitosan and chitosan-CMC solutions were coated onto the patterned gold layer using an electrochemical deposition method as shown in figure 1. The electrochemical deposition was carried out by dipping the substrate in the solution. The dipping process was performed under certain supplied voltage. In this case, ions which are sourced from the solution moved towards the electrode where cations moved towards the cathode and anions moved towards the anode. Thus, the chitosan solution was deposited onto substrate surface. Finally, the coated wet film was annealed at 205°C in a vacuum oven (Model: Memert) for 20 minutes.

![Figure 1. Illustration of electrodeposition process.](image_url)
2.3. Characterization
The chitosan and chitosan-CMC solutions were examined using PSA to see the particle size of the solution. The surface morphology of chitosan and chitosan-CMC films was investigated using Optic Microscope. Thermal property of the films was determined using DTA. Meanwhile, in order to see the functional group of chitosan and chitosan-CMC film was done using FTIR.

2.4. Electrical Testing
In the operation, chitosan and chitosan-CMC film sensors were placed into a chamber, equipped with positive and negative aluminium electrodes. Both electrode points were connected to a high resolution multimeter. Then, the sensors were exposed to acetone gas with concentration 0.1, 0.5, 1, 5, 10 and 50 ppm, respectively.

3. Results and Discussion
Particle distribution measurement was conducted after the solution was kept in normal air for ± 24 hours. Figure 2 showed particle sizes in the solution were 7081.33, 6458.25, 5890.74, 5371.74 and 4678.59 nm for pure chitosan, chitosan-0.01 g CMC, chitosan-0.05 g CMC, chitosan-0.1 g CMC, and chitosan-0.5 g CMC, respectively. It can be clearly seen that the addition of CMC to the solution does not only reduce the particle sizes of the chitosan solution but also keep the chitosan solution is not separated from the solvent even is kept for a long time.

![Figure 2](image)

**Figure 2.** The particle size distribution solution of (a) pure chitosan (b) chitosan-0.01 g CMC (c) chitosan-0.05 g CMC (d) chitosan-0.1 g CMC (e) chitosan-0.5 g CMC.

The result was different when compared to chitosan solution without CMC which tend to be unstable indicated by different particle sizes produced in the measurement. Differences in particle size have declare inhomogeneity of the solution which occur by many factors and one of them because of the separation between the solvent and chitosan as a solute during the solution was kept in normal air.

The morphology of chitosan and chitosan-CMC films were observed using an optical microscope with a magnification of 500 x as shown in figure 3. It can be concluded that the chitosan-CMC solution has successfully deposited on the surface of the gold layer to produce chitosan-CMC films. The formed film layer showed no colour or clear with a texture vary from a uniform without pitting or impurities to the rough or uneven surface.
Figure 3. Surface morphology of (a) pure chitosan (b) chitosan-0.01 g CMC (c) chitosan-0.05 g CMC (d) chitosan-0.1 g CMC (e) chitosan-0.5 g CMC film.

Uneven surface on chitosan film without the addition of CMC was characterized by streaks of particles due to non-homogeneous particle distribution. While the chitosan-0.01 g CMC and chitosan-0.05 g CMC films started to show the homogeneous/uniform surface. The increased stability of the solution with the addition of CMC became the basis of the formation of the uneven surface. On other hand, chitosan-0.1 g and chitosan-0.5 g CMC films produced uneven surface. This is because the increased viscosity of the chitosan solution by the increased number of CMC also increases the magnitude of electrochemical deposition voltage. In line with this condition produced the rough film surface.

Figure 4 shows the thermal property measurement results of the film which were determined using DTA. DTA testing results of the chitosan and chitosan-CMC films showed change thermal conditions through the three stages indicated by the produced peaks. Changes of the peak occur due to changes of chemical reaction and followed by changes in temperature.
Figure 4. DTA analysis for the chitosan and chitosan-CMC films.

Figure 4 described the DTA analysis for the chitosan and chitosan-CMC films. It was clearly shown that the first peak for the thermal change process began at a temperature of 105 – 120 °C which indicate an endothermic process. The maximum peak at 270 – 285 °C was the phase of thermal changes that mark the exothermic reaction in which the molecular chains of constituent film began to break up. It can be concluded that the addition of CMC into chitosan affects the thermal property of the films which indicated by increasing of chitosan-CMC films although the changes are not significant. The high solubility of chitosan with increasing CMC means that chitosan molecular bonds are getting stronger so that it takes a higher temperature to break the bond chains.

Meanwhile, Figure 5 showed FTIR spectra of chitosan and chitosan-CMC films. In the IR spectra of pure chitosan film appeared absorption band at wave number of 3273 cm\(^{-1}\) which was overlap between vibration ranges of -OH and -NH groups. Absorption band at wave number of 2881 cm\(^{-1}\) showed the C-H stretch vibration of alkanes was reinforced by the emergence absorption at wave number of 1408 cm\(^{-1}\). IR spectra of chitosan also raised the vibration of C=O of secondary amide at wave number of 1636 cm\(^{-1}\) and the vibration of -NH secondary amide at wave number of 1556 cm\(^{-1}\). Absorption band of the range of C-H asymmetric of CH\(_3\) appeared at wave number of 1375 cm\(^{-1}\) with a lower intensity and vibration range of the C-N amine identified at wave number of 1322 cm\(^{-1}\) and 1261 cm\(^{-1}\) at a lower intensity as well. Sharp absorption band of C-O asymmetric was identified at wave number of 1152 cm\(^{-1}\). Sharp absorption band at wave number of 1069 cm\(^{-1}\) and 1021 cm\(^{-1}\) was vibration of C-O primary alcohol. Vibration of CH\(_3\) appeared on the wave of 895 cm\(^{-1}\).

These results were compared with chitosan films with the addition of CMC mass variation. Basically, the IR spectra showed relatively similar functional groups. This is due to the presence of CMC does not significantly alter the chemical structure of chitosan film. Changes in the IR spectra of chitosan films were shown in the addition of 0.1 g and 0.5 g CMC. The addition of CMC to the chitosan as the increasing of new absorption band which is the extension of the absorption bands of pure chitosan as a main ingredient film. As the emergence of the range NH of the amide at wave number 2349 cm\(^{-1}\) and 1974 cm\(^{-1}\), vibration formation of NH\(_2\) of the primary amide that appeared at wave number 713 cm\(^{-1}\) on the sensor with pure chitosan and 708 cm\(^{-1}\) on the sensor with CS-0.01 g CMC and shifted to a wave

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**Figure 4.** DTA analysis for the chitosan and chitosan-CMC films.
number of 696 cm\textsuperscript{-1} on the sensor CS-0.05 g CMC, 657 cm\textsuperscript{-1} on the sensor with CS-0.1 g CMC and 662 cm\textsuperscript{-1} on the sensor CS-0.5 g CMC.

These results indicate that the addition of CMC into the chitosan from 0.01 g to 0.05 g does not provide significant structural changes in the film chitosan, but only having a function as additives for the improvement purpose. While the addition of 0.1 g and 0.5 g CMC begins to show a change in the structure of chitosan films. It is characterized by the emergence of new absorption band describing CMC functional group which means that the CMC is not functioning as additional substances such as the original purpose of the use of the CMC.

![Figure 5. FTIR analysis of the (a) pure chitosan (b) chitosan-0.01 g CMC (c) chitosan-0.05 g CMC (d) chitosan-0.1 g CMC (e) chitosan-0.5 g CMC film.](image)

In our previous work, it has been successfully proven that the chitosan film sensors responded the presence of acetone vapour which was indicated by fast response, complete recovery and good stability [32, 33]. However, the improvement of chitosan films is still necessary due to the poor surface, low repeatability and reproducibility. By modifying chitosan films with the addition of CMC, the better results were shown indicated by sensor characteristics in figure 6-8.

Characteristics of chitosan based sensor were observed by exposing chitosan film sensor to acetone gas with different concentrations of 0.1, 0.5, 1.0, 5.0, 10.0 and 50.0 ppm. Figure 6 shows clearly that the greater the concentration of acetone gas exposed, the greater the change in the voltage value of the chitosan and chitosan-CMC films, the same results by Chang Su, etc. [34]. This is due to the greater the concentration of acetone gas exposed, the more the amount of gas that interacts with sensitive material on the surface of sensor. The graph also described that the entire sensor showed a fast response where the sensor began to respond to acetone gas since the early second (0 second) of testing. In this case, the
amine group (-NH) and the hydroxyl group (-OH) of chitosan as a main ingredient of film fabrication have important role to increase the sensor reactivity to interact with the acetone gas. Thus, the sensor is able to respond properly acetone gas.

![Figure 6. Response and recovery time of chitosan and chitosan-CMC film sensors.](image)

From the curve in Figure 6, response cycle may be also determined and recovery time of chitosan film sensor can be obtained. The results showed that the sensors of pure chitosan, chitosan-0.01 g CMC and chitosan-0.05 g CMC films only took 3 minutes for recovery after being exposed. While the sensors of chitosan-0.1 g CMC and chitosan-0.5 g CMC required a longer time for the recovery. This is due to the condition of the uneven film surface which allows retention of acetone to evaporate from sensor surface.

![Figure 7. Sensor repeatability based on (a) pure chitosan (b) chitosan-0.01 g CMC (c) chitosan-0.05 g CMC (d) chitosan-0.1 g CMC (e) chitosan-0.5 g CMC tested under various concentration of acetone gas.](image)
The sensor repeatability is determined by exposing each sensor to different acetone gas concentrations which are in normal air and under acetone gases of 0.1, 0.5, 1.0, 5.0, 10.0 and 50.0 ppm with five times repetition. Among five sensors, chitosan-0.05 g CMC film sensor provided a significant output voltage for each different acetone concentration. In normal condition, sensor output voltage \( V_{out} \) ranged from 200-250 mV. Under acetone exposure of 0.1-0.5 ppm, \( V_{out} \) ranged from 251-300 mV, while under acetone exposure of 1 ppm exhibited that \( V_{out} \) ranged from 301-350 mV. When exposed to 5 ppm acetone, it was found that \( V_{out} \) ranged from 351-400 mV and finally, the exposure of 10 ppm acetone resulted in the range of \( V_{out} \) between 400-450 mV. Compared with the others, pure chitosan and chitosan-0.01 g CMC film sensors provided lowest output voltages, meanwhile chitosan-0.1 g CMC and chitosan-0.5 g CMC film sensors evidenced highest output voltages. This results show the ability of pure chitosan and chitosan-CMC film sensors to differentiate acetone concentrations.

Besides that, the sensor displayed the stability during the measurement, indicated by no fluctuation of the increase in output voltage values when the sensor was exposed to acetone gas. Compared to pure chitosan film sensor, the chitosan-CMC based film sensors showed better stability during the measurement, meaning that the addition of CMC has led to an improvement of sensor characteristics. Among the entire sensors, chitosan film sensor with the addition of 0.05 g CMC showed the most stable measurement results.

![Figure 8. STDEV showing reproducibility of each sensor.](image)

Sensor reproducibility was observed by exposing five sensors with the same composition to various concentrations of acetone. The existence of CMC in the chitosan films give a good effect on sensor reproducibility evidenced by the output voltage values are relatively similar for each other. Chitosan-0.05 CMC film sensor shows most excellent reproducibility reinforced by the STDEV value in figure 8. This indicates that the addition of 0.05 g CMC has a significant effect on the physical condition of this film.

While the lifetime of chitosan and chitosan-CMC film sensors were evaluated every week. As shown in Figure 9, the chitosan and chitosan-CMC film sensors operated well for 8 months since the maximum output voltage values tend to be the same in every week. This indicates that all different sensor compositions have the good lifetime.
Figure 9. Life time of sensor when exposed to (a) wet air (b) 0.1 ppm (c) 0.5 ppm (d) 1.0 ppm (e) 5.0 ppm (f) 10.0 ppm acetone for every week.

4. Conclusion
In this work, acetone sensors based on chitosan have been successfully modified by adding CMC into chitosan solution with the variation of 0.01, 0.05, 0.1 and 0.5 g. Based on the measurement results, chitosan-0.05 w/v CMC has the best physical and electrical properties such as homogenous surface, high thermal properties, fast response, complete recovery, excellent reproducibility, good repeatability and lifetime. Thus, the addition of CMC has improved the performance of chitosan based acetone sensors.

References
[1] Mohammad Z, Therese H, Oksana B, Henry L and Howard W.T 2013 J. Mech. Behav. Biomed 20 217.
[2] Dmitriy B, Bo M and Harald K 2014 J. Biomacromolecules 15 2246.
[3] Haleh Ji, MirKhaliliP, Mohammad A and Hadi A 2016 Int. J. Biol. Macromol 92 461.
[4] S. Paydar, M.H. Shariatand S. Javadpour 2016 J. Alloys. Compd 682 239.
[5] KumirskaJ, Weinhold M. X, Thöming J and Stepnowski P 2011 J. Polymers 3 1875.
[6] Shaolin W, Zan W, Xianliang Z and Xin W 2017 J. Mater. Lett 186 17.
[7] Bhawna S, El Barbary H, M. Wes S and Barakat M 2016 J. Carbohydr. Polym 151 780.
[8] Ivo P, Oksana K, Máksym P, Aleksei K, Aleksandr S, Anatoly S, Sergei D and Temenuzhka Y 2016 J. Carbohydr. Polym 151 770.
[9] Javiera F, Davinia C, Angel C, Olga D and Franco P 2016 J. LWT-Food. Sci. Technol 72 206.
[10] Itsaso L, Pedro G, Sara C and Koro de la C 2013 J. Clean. Prod 41 312-313.
[11] Lambertus A.M, Rutger J.I, Frans H.J and Carmen G 2015 J. Carbohydr. Polym 116 237.
[12] Maria R, Amalia C, Elisabeta E, Elena G, Paul P, Mona E, Jan T, Morten S, Raluca N and Cornelia V 2016 J. Compos. Part. B. Eng 102 113.
[13] Fatemeh H, Mehdi R, Mohammad E, Reza B, Daryoosh V, Hari K and Lobat T 2016 J. Mater. Sci. Eng. C. Mater. Biol. Appl 65 338.
[14] V. Mini, Kamath A, S. Raghu, C. Sharanappa and H. Devendraappa 2016 J. Mater. Chem. Phys 170 91.
[15] Amir Azarniya, Niloofar Eslahi, Nafiseh Mahmoudi and Abdolreza Simchi 2016 J. Compos. Part. A. Appl. Sci. Manuf 85 113.
[16] E. Prokhorov, G. Luna-Bárcenas, J.B. González-Campos, Yu. Kovalenko, Z.Y. García-Carvajal and J. Mota-Morales 2016 J. Electrochim. Acta 215 600.
[17] Ubonrat S and Waranya V 2016 J. Food. Hydrocoll 61 695.
[18] Qiang Z, Jinwen Q, Quanfu A, Congjie G, Zhangliang G and Huangtao J 2009 J. Memb. Sci. 333 68.
[19] Ning C, Chao L, Chao H, Xiaogang L, Liang S, Yanan X and Faquan Y 2016 J. Appl. Surf. Sci 369 492.
[20] Melis E, Emin E, Zehra O and Mustafa Ç 2016 J. Carbohydr. Polym 151 314.
[21] Débora G, Linus P.F, Santiago S and Gustavo F.S 2016 J. Vib. Spectrosc 87 8.
[22] Peter D, Junjie H, Stephan T, Gregory F, Liangli Y and Reza G 2009 J. Sensor. Actuat. B. Chem 138 64-70.
[23] Dan D, Jiawang D, Jie C and Aidong Z 2007 J. Electroanal. Chem 605 53-60.
[24] S. Anandhavelu and S. Thambidurai 2013 J. Electrochim. Acta I 90 194.
[25] Zafer Y, Yoldas S, Ibrahim Ş, Kutlay S, Ömer M and Mehmet S 2016 J. Compos. Part. B. Eng 98 281.
[26] Huanle C, Xiaorong H, Enmin C, Shan W, David J, Shilin L, Bin L and Yan L 2016 J. Food. Hydrocoll 61 662.
[27] Han N, Ji S, Su Y and Keun-Hong P 2015 J. Carbohydr. Polym 122 265-266.
[28] Sudarat S, Chalermchai P, Titipun T and Somchai T 2015 J. Appl. Surf. Sci 356 973.
[29] Siqueira, Brochier S and E. Mauret 2015 J. Ind. Crops. Prod 72 87-88.
[30] A. Hiroki, H.T. Tran, N. Nagasawa, T. Yagi and M. Tamada 2009 J. Radiat. Pyhs. Chem 78 1076.
[31] Ahmed M, Samah M, Hoda S, Heba H and Alain D 2016 J. Carbohydr. Polym 151 9.
[32] Tulus I, Irwana N, Sabar D, Khairel R and Zainal A 2013 J. Sensor, Actuat. B. Chem 177 522-528.
[33] Tulus I, Zainal A, Khairel R, Irwana N and Ainnie S 2013 J. Sains. Materi. Indonesia Special Edition.
[34] Chang S, Changbai L, Li L, Mucui N, Haiying L, Xiaoqing B, Lili L and Xiaochi 2014 J. Appl. Surf. Sci 314 933.