The effect of Acetic Acid Ratio in The Electrodeposition Process of Chitosan/ZnO

Saisa1,2, Harry Agusnar1,*, Zul Alfian1 and Irwana Nainggolan1*

1Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Sumatera Utara, Medan, Indonesia
2Department of Chemical Engineering, Faculty of Engineering, Universitas Serambi Mekkah, Banda Aceh, Indonesia

*harryagusnar@usu.ac.id, irwana@usu.ac.id

Abstract. Chitosan is a material that sensitive to the environmental changes and has been used in the developing of sensor. The fabrication of chitosan/ZnO composite was prepared using the electrodeposition method over PCB plate. ZnO content was variated to be 10, 20 and 30 wt.%. Also the composite was prepared in acetic acid 2 and 5%. The aim of the present study is to evaluate the preparation process of chitosan/ZnO composite with acetic acid concentration as the independent variable in this research. The XRD data showed a peak at 2θ 30.8° that confirmed the presence of ZnO in the composite. The FTIR spectra showed the presence of ZnO can be found at 550 cm⁻¹ and the acetic acid concentration influenced the intensities of the composites. The surface morphology of composite that prepared using acetic acid 2% has a smoother surface than the composite that prepared using acetic acid 5%. The voltage response of chitosan/ZnO composite that prepared using acetic acid 5% showed the highest value (0,1525 V) than the composite that prepared using acetic acid 2% (0,0581 V).

1. Introduction

Nowadays, sensor technology become an interesting issue among the researchers. The new kinds of sensor, matrix of sensor, the new detection method of sensor continue to be developed to obtain a sensor that automatic, safe and comfort to use [1]. The developing of sensor today mostly used the material in nanosized to improve the performance of sensor.Chitosan nanoparticle as sensor has been widely utilized in many applications, such as to measure the soil moisture [2], to measure acetone concentration [3], to detect actin in the cancer patient [4], to measure hydrogen peroxide using non-enzymatic technique without supporting electrode [5].

Chitosan composite and ZnO nanoparticle are two kind materials that difficult to dissolve in water, slightly soluble in hydrochloric, nitric and acetic acid of 1-2%, and easily soluble in formic acid 0.1-0.2% [6] [7]. Many studies described the solubility of chitosan in acetic acid was found at 1-2% [6] [8], in other study Fu [8] dissolved chitosan using acetic acid 10% with the presence of methanol. The amino and hydroxyl group of chitosan have an influence to the chemical and physical properties, such as chitosan has a high reactivity, chitosan called as cationic polymer, chitosan can be used as ion exchange to ligate or adsorb heavy metal [9]. Unmodified chitosan is very sensitive to the environmental changes and has low mechanical properties [10]. To improve the properties of chitosan the addition of additives is needed. Due to that reason, the aim of the present study is to evaluate the
preparation process of chitosan/ZnO composite with acetic acid concentration as the independent variable in this research.

2. Methodology
Chitosan (medium molecular weight) and zinc oxide (~99% of purity) were obtained from Sigma-Aldrich. Acetic acid glacial was purchased from Merck. All chemicals were used without further purification.

2.1 Preparation of chitosan’s solution
One gram of chitosan was dissolved in 100 mL of acetic acid (2 and 5% (v/v)). The solution was stirred at room temperature for 24 h until the homogenous solution was obtained.

2.2 Preparation of ZnO solution
Some amount of ZnO (0.1 g) was dissolved in 100 mL of acetic acid (2 and 5% (v/v). The solution was stirred at 70°C for 24 h until the homogenous solution was obtained.

2.3 Preparation of Chitosan/ZnO
The prepared solution of chitosan and ZnO was mixed with the following ratio (v/v), such as 90:10, 80:20 and 70:30. The final volume of the mixed product was 25 mL. The mixing process was conducted for 1 h with an assumption the obtained solution has been homogenous.

2.4 Electrodeposition of Chitosan/ZnO
The electrodeposition process of chitosan/ZnO solution was performed with the following condition. PCB plate was dipped into chitosan/ZnO solution which has been electrified (2.5 V). The presence of bubble in the cathode was an indicator of the electrodeposition was started. After 5-7 minutes the fabrication of chitosan/ZnO film was stopped, and the PCB plate was dried in oven at 105°C for 30 minutes. At the end the voltage response of the as-prepared chitosan/ZnO film was measured by 10, 20 and 30 wt.%

2.5 Characterization of chitosan/ZnO
The as-prepared chitosan/ZnO film was characterized using FTIR (BRUKER HYPEROIN 3000) to determine the change of functional group during the process electrodeposition, SEM (Hitachi TM3000) to evaluate the morphology chitosan/ZnO film and XRD (BRUKER EIGER2 R 500K Detector) to confirm the presence of ZnO in the chitosan/ZnO film after fabrication.

3. Results and Discussion
The XRD analysis was performed to confirm the presence of ZnO in the composite of chitosan/ZnO after facrication process through electrodeposition technique. In the Fig.1 can be seen the XRD spectra of chitosan/ZnO that compared to the ZnO signal using Match! V2.0. The XRD spectra showed the ZnO still can be found in the composite of chitosan/ZnO although it presence in the low intensities. The confirmation of ZnO can be seen in the 2θ at 30,8°.

Figure 1. XRD spectrum of chitosan/ZnO
The addition of ZnO into the electrodeposition process of chitosan is one method that can improve the performance of chitosan itself as sensor. Based on the SEM analysis, Fig. 2a showed the morphology of chitosan/ZnO with 2% of acetic acid which has smooth surface and the filler (ZnO) has a good distribution in the matrix of chitosan. In other hand, Fig. 2b showed the film of chitosan/ZnO that prepared with acetic acid 5%, which has a different surface morphology. There is a lot of pores presence in this specimen that caused by the presence of bubble (foam) during the formation of film. The increase of acid concentration can be a reason of this phenomenon because acid concentration is a key factor in the electrodeposition process. A study about the acid concentration to the solvation process of chitosan and its effect to the electrodeposition process has been conducted [11].

Figure 2. Surface morphology of chitosan/ZnO film with acetic acid (a) 2% and (b) 5%

The FTIR analysis also conducted in this research, Fig. 3 showed the FTIR spectra of chitosan/ZnO film that prepared with acetic acid 2 and 5%, respectively. Both spectra showed a no significant difference on the chemical shift but the different of those peaks can be observed on the intensities of each signal. In the Fig. 3, the presence of hydroxyl (-OH) and amine (-NH) group can be found at 3261 cm\(^{-1}\). The stretching vibration of carbonyl and amine group of chitosan was appeared at 1554 cm\(^{-1}\). The presence of asymmetric hydroxyl and amine group was appeared at 3261 cm\(^{-1}\). The other peaks also appeared at 1402 and 1019 cm\(^{-1}\) that represent the stretching vibration of C-N and asymmetric C-O bonding. This data also supported by the study of [12].

Figure 3. FTIR spectrum of chitosan/ZnO film with acetic acid 2 and 5%
Electrodeposition process has been performed using PCB plate in the chitosan/ZnO solution. The presence of bubble or foam in the cathode means the electrodeposition has occurred. The voltage response of the as-prepared chitosan/ZnO film that prepared in acetic acid 2 and 5% was discussed as the effect of chitosan and ZnO ratio (10, 20 and 30%).

Based on Fig. 4a and b, the highest voltage response was showed at 20% of ZnO content with value 0,0581 and 0,1525 V for the composite that prepared with 2 and 5% of acetic acid, respectively.

4. Conclusion
In summary, during electrodeposition process acetic acid ratio affected on the color and perform of the as-prepared chitosan/ZnO film. It can be concluded as below:
1. The solubility of chitosan and ZnO in acetic acid is depended by the acid concentration, the higher the acid concentration, the solubility of those materials become low.
2. The surface morphology of chitosan/ZnO composite that prepared using acetic acid 2% has smoother surface than the composite that prepared using acetic acid 5%.
3. After the electrodeposition process, chitosan/ZnO composite that prepared using acetic acid 5% showed the highest value of voltage response (0,1525 V) than the composite that prepared using acetic acid 2% (0,0581 V).

Acknowledgments
Author thanks the Indonesia Endowment Fund for Education (LPDP) for the Doctoral Scholarship and the financial support for conducting the research.

References
[1] M. Djamal, E. Sanjaya, R. Wirawan, and A. Hartono, “No Title,” in Prosiding Seminar Kontribusi Fisika, 2011.
[2] T. I. Nasution, I. Nainggolan, D. Dalimunthe, M. Balyan, R. Cuana, and S. Khanifah, “No Title,” in IOP Conf. Ser. Mater. Sci. Eng. 309 12080, 2018.
[3] T. I. Nasution, R. Asrosa, I. Nainggolan, M. Balyan, R. Indah, and A. Wahyudi, “No Title,” in IOP Conf. Ser. Mater. Sci. Eng. 309, 2018.
[4] C. Sun et al., “No Title,” Sensors, vol. 18, 2018.
[5] A. Arena, G. Scandurra, and C. Ciofi, “No Title,” Sensors, vol. 17, 2017.
[6] M. Abdolrahimi, M. Seifi, and M. Zaden, “No Title,” Chinese J. Phys., vol. 56, no. 1, pp. 221–230, 2018.
[7] A. Purwanti and M. Yusuf, “No Title,” in Seminar Nasional Rekayasa Teknologi Industri dan Informasi, 2013.
[8] T. Furuike, D. Komoto, H. Hashimoto, and H. Tamura, “No Title,” *Int. J. Biol. Macromol.*, vol. 104, no. Part B, pp. 1620–1625, 2017.

[9] C. Nugroho, N. Nurhayati, and B. Utami, “No Title,” *J. Mol.*, vol. 6, pp. 123–136, 2011.

[10] H. Zhang, Y. Sanyue, S. Lingling, Z. Yiwen, and Z. Yanyun, “No Title,” *Int. J. Biol. Macromol.*, vol. 96, pp. 334–339, 2016.

[11] Balyan, “No Title,” Universitas Sumatera Utara Program Pasca Sarjana, 2017.

[12] T. Nasution, R. Asrosa, Y. Machrina, I. Nainggolan, M. Balyan, and R. Rumansyah, “No Title,” 2017.