Study on chitosan film properties as a green dielectric

I Nainggolan\textsuperscript{1,3,4*}, T I Nasution\textsuperscript{1,2,5}, S R E Putri\textsuperscript{1}, D Azdena\textsuperscript{1}, M Balyan\textsuperscript{2,5} and H Agusnar\textsuperscript{1,4}

\textsuperscript{1}Physics Department, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia
\textsuperscript{2}Centre of Excellence for Sensor Systems and Technology, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia
\textsuperscript{3}Centre of Excellence for Green Chitin and Chitosan, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia
\textsuperscript{4}Chemical Department, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia
\textsuperscript{5}Integrated Laboratory, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia

*Email: ikhsan_05@yahoo.com

Abstract. Chitosan film dielectrics to produce an electrostatic capacitor were prepared by the solution cast technique. The charging and discharging of the capacitor were done using RC series circuit with DC voltage supply because chitosan has bipolar properties. First testing was by varying supply voltage of 1, 3, 5, 10 and 15 V, respectively, and could be determined that the most effective voltage for chitosan film can be well polarised is 5 V. The results of second testing for the use of 5 V supply showed that the capacitance of a chitosan film capacitor decreased with the increase in load value. For loads of 100, 1K, 10K, 100K and 1M Ω, the capacitance values of the chitosan film capacitor were 3.1725, 0.4136, 0.05379, 0.007917 and 0.001522 F, respectively. It was also found that the increase in voltage of the capacitor at charging process was faster for the lower load. Therefore, the research result has corresponded to the general formula that used to calculate the capacitance value and thus, the biopolymer chitosan has potential as a sustainable green dielectric.

1. Introduction

Natural polymers are becoming the new belle in the development of electronic devices because they come from renewable sources that are reproducible. While synthetic polymers begin to anxiety about the availability of the source of its raw materials, coupled with its poor degradability [1]. Among the most popular electronic components based natural polymer today are capacitors or supercapacitors, these passive storage components are beginning to experience renewal in their constituent parts. Various natural polymers such as cellulose [2], chitosan and starch [3] with the addition of dopant and plasticizer have been developed in the fabrication of solid electrolyte materials. The combination of two polymers was done by many researchers because they are capable to produce solid electrolyte with better mechanical and chemical properties [4].
In this study, chitosan was chosen as a dielectric material for electrostatic capacitor applications because have many interesting properties among others are biodegradable, biocompatible, biofunctional and low cost [5-7]. Moreover, chitosan is ranked second largest as the most abundant polymer in nature [8]. Chitosan has a bipolar charge, which is a negative charge in the carboxylate group and a positive charge in the NH group [9]. The existence of these two groups makes chitosan film can be placed between two metal plates to produce a bipolar-type capacitor. This is due to the chitosan film is capable to act as a dielectric material that can experience dipole induction when an electric field is applied.

So far we know, the research on the potential of pure chitosan as a dielectric material for electrostatic capacitors has not been found. However, the chitosan-Carrageenan-H₃PO₄-PEG [10] and Poly (Vinyl Alcohol) -Chitosan-Ammonium Nitrate (NH₄NO₃) - Ethylene Carbonate [11] as solid electrolyte materials for supercapacitor applications have been done by A.K.Arof and his team. In this study, the ability of chitosan film to function as a dielectric in electrostatic capacitor applications is explained from charging and discharging test results by varying the supply voltage to obtain the optimal operational voltage and loads to compare the dielectric capability of chitosan film in saving electricity.

2. Experimental
The sample was prepared using the solution cast technique by stirring 1.5 grammes of chitosan powder in 50 mL 1% (v/v) acetic acid solution. The chitosan powder was purchased from Sigma-Aldrich with the type of medium molecular weight and deacetylation rate of 75% - 85%. While the acetic acid was purchased from EMD Millipore. The stirring process was done using a Scilogex magnetic stirrer with the rotation speed of 300 rpm for 6 hours at room temperature (23 ± 2 °C). After the stirring process, the homogeneous solution was poured into a Normax Petri dish and then, dried in the Digital Oven (Memmert UN 55) at 60 °C for 16 hours. The dried chitosan thick film was cut into a smaller thick film with the dimension of 1.8 x 1.8 cm².

The experiment setup was carried out using charging and discharging test. The Chitosan film with a surface area of 3.24 cm² and a thickness of 200 μm was placed between two copper electrodes in parallel to produce an electrostatic capacitor setup. Charging-discharging test was performed by using series RC circuit where the supply voltage was varied from 1, 3, 5, 10 and 15 V. The measurement data was recorded using a digital multimeter Hydra Series III fluke 87 V. Hereafter, the charging-discharging test was done at voltage value of 5 V by varying the load value of 100, 1K, 10K, 100K and 1M Ω. The dielectric chitosan film was characterised using Differential Scanning Calorimetry (SDT Q100) to determine the temperature of the transition glass, the chitosan film was heated from room temperature to 500 °C with a heating rate of 10 °C/minute. While, the Functional group analysis was conducted using a Fourier Transform Infrared Spectroscopy (SHIMADZU model IRPrestige 21).

3. Results And Discussion
Figure 1 shows the charging and discharging processes of dielectric film chitosan in electrostatic capacitor setup that are done with series RC circuit. Variation of supply voltage aims to see how the value of the voltage that can be accepted dielectric without reducing the ability dielectric in storing the charge.
e) Figure 1. The charge and discharge testing of dielectric chitosan films using a series RC circuit at supply voltages of (a) 1 V, (b) 3 V, (c) 5V, (d) 10 V and (e) 15 V.

In every supply voltage variation, the chitosan dielectric film in the electrostatic capacitor setup shows the increase and decrease in the current and voltage of the charging process called the transient period, this is the state when an object undergoes a sudden change under the influence of current or voltage. In the dielectric, these changes sometimes can lead to fatal damage that is the breaking of the chemical bond of dielectric materials that under special conditions (such as C = O group of primary amide on the chitosan film) can cause the free electrons are formed which can lead to dielectric failure. Next, in a few seconds the dielectric chitosan film in the electrostatic capacitor setup experiencing steady state, this condition generally indicates that the capacitor is fully charged. A stable voltage and current value from the beginning of the capacitor entering steady state until the specified charging time are over indicate that the transient state creates no damage to the bonding of the chitosan molecule. Then in the discharging process, the transfer of charge on load is so fast this is seen from the sharply decreasing graph. This shows that the chitosan film molecule has a short response time. Some anomalies occur in samples 4 and 5 on variations in supply voltages of 10 and 15 volts, indicating that there is a breaking of the functional group of chitosan molecules when the voltage enters the range of 10-15 volts. Therefore it can be concluded that the 5 volt voltage is the most appropriate voltage for dielectric to work with the optimum, this is proven by calculating the value of the charge that can be stored by the capacitor after the charging process (Figure 2)
The DSC analysis result (Figure 3) shows the endothermic peak value of $T_g$ is 103.681°C and the exothermic peak value $T_m$ is 297.737°C, indicating that the dielectric chitosan film has good thermal resistance. At the charging process, the dielectric chitosan film will experience an increase in temperature due to the given voltage. The temperature effect can cause vibrations in the lattice causing the electrons in the atoms to get extra energy so that the electrons escape from the lattice. This process is referred as the ionization event and then, these free electrons collide and get trapped in the skin of the atom with a higher electrical potential energy than the energy it has. This state causes a chemical change in the dielectric material resulting in deterioration of the dielectric electrical properties that called macroscopic electrical damage, in which dielectrics made from natural polymers such as chitosan is susceptible to this condition. Under allowable voltage conditions, repetition effects may also cause macroscopic electrical damage. In a situation where dielectric can not long withstand the applied voltage due to too many free electrons in the material, it will eventually make the dielectric lose its insulating properties which make it be a dielectric failure.

The absorption band at wavenumber 3572 cm$^{-1}$ is the vibration of the overlapping $-\text{OH}$ group range with $-\text{NH}$ of the primary amine, whereas the absorption band at wavenumber 1593 cm$^{-1}$ is $-\text{NH}$ vibration of the secondary amine (Figure 3). Both functional groups are the main actors in the polarization of dielectric film chitosan. During the charging process, the negative charge of an electric current on one of the copper plates attract the positive charge in the NH group in the chitosan film molecule. This causes the negative charge in the carboxylate group to shift towards the positive charge of the electric current on the other plate.

Figure 2. The charge stored after the charging process

Figure 3. DSC analysis of chitosan film

Figure 4. FTIR analysis of chitosan film
capacitance value is decreased when load value is increased (Table 1). This result has corresponded with the general formula of capacitance in the RC circuit,

$$C = \frac{\tau}{R \ln \left( \frac{IR}{E} \right)}$$  \hspace{1cm} (1)

where it looks that the addition of the load value is inversely proportional to the value of the capacitance.

| Table 1. Change the value of the capacitance at each load value |
|-----------------|-----------------|
| $R$ (Ω) | $C$ (F) |
| 100 | 3.1725 |
| 1000 | 0.4136 |
| 10000 | 0.05379 |
| 100000 | 0.007917 |
| 1000000 | 0.001522 |

4. Conclusion
Chitosan film that is prepared by the solution cast technique can be used as a green dielectric to produce an electrostatic capacitor. The optimal operational voltage of dielectric chitosan film for storing the most amount of electrical charge is 5 V DC. Therefore, the chitosan film can be applied as an environmental friendly dielectric material with low supplied voltage consumption.

5. Acknowledgements
We would like to acknowledge the funding and support from the Centre of Excellence for Green Chitin and Chitosan Universitas Sumatera Utara.

6. References
[1] Shukur M F, Ithnin R and Kadir M F Z 2014 Electrochim Acta 136 204–216
[2] Shuhaimi N E A, Teo L P, Woo H J, Majid S R and Arof A K 2012 Polym. Bull 69 807–826
[3] Teoh K H, Lim C S, Liew C W, Ramesh S and Ramesh 2015 Ionics 21 (7) 2061–2068
[4] Mahendran O and S Rajendran 2003 Ionics 9 282–288
[5] Dutta P K, Dutta J D and Tripathi V S 2004 J Sci Ind Res 63 20 – 31
[6] Aldana A A, Toselli R, Strumia M C and Martinelli M 2012 J. Mater. Chem. 22 22670- 22677
[7] Brown M A, Daya M R and Worley J A 2009 J. Emerg. Med. 37(1) 1–7
[8] Kumar M N V R 2000 React. Funct. Polym. 46 1–27
[9] Bansal V, Sharma P K, Sharma N, Pal O P and Malviya R 2011 Adv. Biol. Res. 5(1) 28–37
[10] Arof A K, Shuhaimi N E A, Alias N A, Kufian M Z and Majid S R 2010 J. Solid State Electrochem. 14 2145–2152
[11] Kadir M F Z and Arof A K 2011 Mater. Res. Innov. 15 sup2, s217-s220