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Properties of Polymer Electrolytes based on Chitosan/Poly(vinyl alcohol) for Lithium Battery Application

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ABSTRACT: *Lithium battery is a commercial battery that is currently widely produced due to its high energy capacity, longer life time, and efficient use, making it suitable for many electronic devices. Unfortunately, the use of liquid electrolyte in lithium ion batteries is particularly vulnerable to leakage, corrosive, and flammable when charging batteries at high temperatures. To solve this problem, various research trends evolved, including research on polymer electrolyte in lieu of liquid electrolytes on lithium ion batteries. Indonesia is an archipelagic country rich in marine products, in which the high consumption of it leaves a huge pile of waste. One of the waste groups is shrimp shell that contains a lot of chitin. Further processing of chitin produces chitosan that has great potential to be use as the major component in polymer electrolyte synthesis. To improve the performance of chitosan-based electrolytes, particularly their ionic conductivity property, the blending of chitosan with poly(vinyl alcohol) (PVA) and $LiClO_4$ was performed. The results show that the polymer electrolyte prepared by blending chitosan, PVA, and $LiClO_4$ has a higher ionic conductivity and mechanical strength rather than a pure chitosan. A maximum ionic conductivity about 4.57 x 10^{-3} S cm^{-1} was produced from polymer electrolytes with 70% chitosan/PVA (90/10) and 30% $LiClO_4$. The increase of ionic conductivity of the blending electrolyte is due to the increasing number of both the amount and the mobility of lithium ion after the addition of PVA and $LiClO_4$. This result was also supported by mechanical data analysis, surface morphology, and thermal data analysis.*

KEYWORD: *chitosan, PVA, $LiClO_4$, polymer electrolyte, lithium battery*

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I. INTRODUCTION

The rapid development of various types of sophisticated electronic devices, such as smartphones, laptops, digital cameras, sensors, and electric vehicles, is currently triggering the increase of energy availability. For easy use and safety reasons, the use of energy sources now leads to the development of eco-friendly rechargeable lithium batteries that enable to cross over wide range of applications. Since being commercialized for the first time by Sony in 1990, a rechargeable liquid electrolyte lithium ion battery, as the first generation of this type, has attracted so much attention mostly due to its high energy and power density. At ambient temperature, the liquid electrolyte placed between the two electrodes of the lithium battery could achieve ionic conductivity in the order of 10^{-3} to 10^{-2} S cm^{-1}, 300-500 charge/discharge cycle life, and excellent electrochemical stability window [1]. However, the use of liquid electrolytes in battery system has high risk of leakage, which can ultimately result in negative impacts on battery reliability and environmental issues. To overcome this problem, a solid electrolyte system based on polymeric materials has been developed to replace the liquid electrolyte. The materials use as polymer electrolyte can be selected and synthesis in various ways, such that it possesses similar properties with that of liquid electrolyte. The polymer electrolyte should also have high mechanical strength, high thermal stability, and due to economic cost reason, they also need to be low cost and easy to produce.

Solid polymer electrolyte used for lithium battery is generally synthesized from poly(ethylene oxide) (PEO) and has shown good ionic conductivity (greater than 10^{-4} S cm^{-1}) at high temperature. Unfortunately, as the temperature decrease, the conductivity obtained from this system drops dramatically even reach the order of 10^{-8} to 10^{-7} S cm^{-1} at ambient temperature. To increase the ionic conductivity, a few works have been done in polymer modification using various types of polymeric and inorganic materials. A good result was reported by Subadevi in 2011, poly(vinylidene fluoride) (PVDF) was blended with poly(ethyl methacrylate) (PEMA), using lithium salt as lithium ion sources, and ethylene carbonate and propylene carbonate as plasticizers. The system showed good transport properties, with the highest ionic conductivity 1.3×10^{-3} S cm^{-1} at 301 K [2]. The problem is, although it has high ionic conductivity near room temperature, the use of this electrolyte tends to be avoided due to the non-degradable polymers involve in the electrolyte, which in turn causes negative effects to the environment [3]. Eventually, the development of polymer electrolyte for lithium battery system is preferably leading to the use of a low cost, high availability, and eco-friendly polymeric materials.

Indonesia as an archipelagic country with two-thirds of its territory in the form of ocean has very abundant marine products. The high consumption of it leaves huge piles of waste, one of the most commonly known is shrimp shell. Shrimp shells contain high content of chitin [4]. Chitin is generally known as a precursor in the synthesis of chitosan, the second largest number of natural polymers after cellulose. Due to its natural abundant availability, low production costs, and environmentally friendly, chitosan is often used as materials for various medical purposes, drug delivery systems, solid polyelectrolytes, surfactants, ultrafiltration, reverse osmosis, and evaporation [1, 5].

Polymer electrolyte from pristine chitosan has low ionic conductivity, thus several modifications need to be done. Previous study had shown polymers such as poly(ethylene glycol) [1], poly lactide [6], poly(vinyl pyrrolidone) [7], polycaprolactone [8], 3–oligomers (aminopropyl) siloxane [9], and plasticizers [10] blended with chitosan could produce electrolytes with better transport properties. Among all the alternative for chitosan modifications, poly(vinyl alcohol) (PVA) with hydroxyl group in the polymer chain has great potential to be blend with chitosan. PVA is chosen here due to its low toxicity, good biodegradable, good ionic conductivity and mechanical stability, and has hydroxyl group that can form good interaction with functional groups in chitosan. Therefore, in this study is focused on studying the properties of polymer electrolyte based on chitosan – PVA as a promising electrolyte for lithium battery. In this paper will be presented the relationship between the ratio of chitosan and PVA in the polymer electrolyte with their transport, mechanical, and thermal stability properties related to its application in lithium battery system.

II. EXPERIMENTAL

Materials and Equipments

All materials in this study were used without further purification. The materials are shrimp shells, sodium hydroxide (NaOH) (Merck), hydrochloric acid (HCl) 37% w/w (Merck), acetic acid (CH_3COOH) 99% w/w (Merck), poly(vinyl alcohol) (PVA) (Merck), and lithium perchlorate ($LiClO_4$) (Merck).

The polymer electrolytes were printed in a Teflon plate. The instruments used for characterization were: Ostwald viscometer for average molecular weight measurement, Bruker Alpha ATR-FTIR for structure analysis, Precision LCR Meter Agilent E4980a for ionic conductivity measurement, Single Fiber Tensile Testing Machine Techno H STEIN 41066 MOENCHENGLADBACH for mechanical analysis, JEOL JSM-6360 Analytical Scanning Electron Microscope and JEOL FINE Sputter Ion COAT JFC-1100 for morphology and membrane cross section analysis, and Thermogravimetric Analyzer STA LINSEIS PT1600 for thermal analysis.

Isolation of Chitin from Shrimp Shells

Isolation of chitin from shrimp shells was carried out in two stages of reaction: deproteination and demineralization. At the deproteination stage, completely clean and dry shrimp shellswas mixed with NaOH 3.5% (w/v) solution with a ratio of 1:10. The mixture was stirred in a68°C water bath for 2 hours, and then filtered to get the residue. The residue was washed with distilled water until neutral and then subsequently dried in a 60°Cvacuum oven for 24 hours. The solid obtained was a protein-free chitin. At the demineralization stage, protein-free chitin was dissolved in HCl 1 M with a ratio of 1:15 (w/v). The mixture was stirred at ambient temperature for 2 hours until no bubble gas formed. The mixture was then filtered and the remaining residue was washed with distilled water until neutral. The residue obtained was dried in a 60°C vacuum oven for 24 hours. The solid obtained after this process was chitin.

Synthesis of Chitosan

Chitin obtained from the demineralization stage was dissolved in NaOH 50%(w/v) solution with a ratio of 1:15. The mixture was stirred in oil bath at 110 °C for 2 hours, and then filtered to get the residue. The residue was washed with distilled water until neutral and then subsequently dried in a 60 °C vacuum oven for 24 hours. Deacetylation stage was carried out twice to obtain high degree of deacetylation of chitosan.

Synthesis of Polymer Electrolytes

Synthesis of polymer electrolytes was initiated by dissolving various compositions of chitosan, PVA, and $LiClO_4$in acetic acid 2% solution. The mixture was stirred for 24 hours at ambient temperature. The polymer electrolytes were obtained from solution casting method, in which a total of 10 mL polymer – salt solution was poured into a Teflon plate. The solution was then kept in ambient temperature condition, in which the solvent could evaporate for 1 week.

Characterization of Chitin, Chitosan, and Polymer Electrolytes

Chitin and chitosan obtained in this study were characterized using FTIR analysis. The degree of deacetylation of chitosan was calculated using baseline method with Domszy & Robert equation:

$$\text{Degree of deacetylation} = 100 - \left(\frac{A1655}{A3450} \text{ x } \frac{100}{1,33} \right)$$

A_{1655} = absorbance at 1655 cm^{-1}
A_{3450} = absorbance at 3450 cm^{-1}
The characterization of polymer electrolytes involved infrared spectroscopy, ionic conductivity measurement, morphology and membrane cross-section analysis, mechanical and thermal stability analysis.

III. RESULTS AND DISCUSSION

Chitosan

The main raw material for the synthesis of chitosan is the cuticle of various types of crustaceans, especially crabs and shrimp which contain high content of chitin. In the cuticle of crustaceans, there are also large amounts of protein and calcium carbonate, in addition of chitin. The interaction between chitin and protein are very strong, thus in general there is also small amount of protein involved in the polysaccharide-protein complex [11].

Isolation of chitin from shrimp shells requires a series of processes that generally aim to eliminate the content of the two main components besides chitin: protein through the deproteination stage, calcium carbonate through the demineralization stage, while small amounts of pigments and lipids disappear gradually during deproteination and demineralization stages. However, the synthesis of chitosan from chitin was carried out through deacetylation process. The chitin and chitosan obtained in this study are given in Fig. 1.

a b

Fig. 1. Synthesis products of: (a) chitin and (b) chitosan

The total weight and yield obtained from the deproteination, demineralization, and deacetylation stages in the synthesis of chitosan from shrimp shells are given in Table 1.

Table 1. Total weight and yield obtained from the synthesis of chitosan

No.	Synthesis stages	Weight (g)	Yield (%)
1.	Deproteination	58.5596	83.44
2.	Demineralization	30.2514	51.66
3.	First deacetylation	22.0005	72.73
4.	Second deacetylation	18.8211	85.55

The structure of chitin and chitosan was examined using FTIR spectroscopy. Generally, both chitin and chitosan have similar structure that differs only in the absorbance of the acetyl group. FTIR spectrum of chitin (Fig. 2) showed significant peaks according to the functional groups contained in its structure: 3482 cm^{-1} and 3262 cm^{-1} (stretching vibration of O-H alcoholic groups and N-H amide groups); 2885 cm^{-1} (stretching vibration of C-H alkanes); 1660 cm^{-1} (C=O amide); and 1551 cm^{-1} (N-H which appears in the fingerprint area).

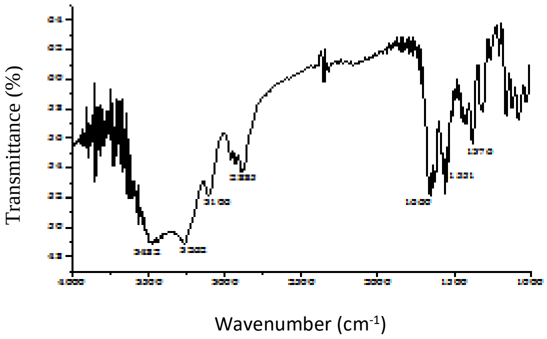

Fig 2. FTIR spectrum of chitin

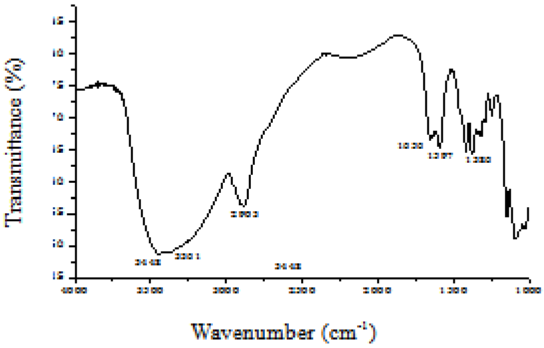

Fig 3. FTIR spectrum of chitosan

The FTIR spectrum of chitosan (Fig. 3) showed the presence of similar peaks with chitin. The difference in both spectrums is only determined by the intensity ratio between the carbonyl absorption peak around 1655 cm^{-1} and N-H absorption peak around 3450 cm^{-1}. In the spectrum of chitosan, the intensity of carbonyl absorption decreases, while the intensity of N-H stretching vibration increases. The main absorption peaks that appear in the chitosan spectrum are: 3448 cm^{-1} and 3361 cm^{-1} (stretching vibration of O-H alcoholic groups and N-H amide groups); 2903 cm^{-1} (stretching vibration of C-H alkanes); 1656 cm^{-1} (C=O amide); and 1597 cm^{-1} (N-H which appears in the fingerprint area).The spectrum is also used to calculate the degree of deacetylation of chitosan using the Domszy & Robert equations. The degree of deacetylation of chitosan obtained in this study was 72.02 % after the first deacetylation. The degree increases to 77.65 % after the second deacetylation.

Polymer Electrolytes

ATR-FTIR Analysis

The ATR spectrum of pristine chitosan, pristine PVA, chitosan with lithium, and chitosan□□□PVA with lithium are shown in Figure 4. In general, the four types of electrolytes have relatively the same absorption peaks position. Pristine chitosan has amine group, O-H group, and C-H alkane group. The addition of lithium salt does not change the position of the absorption peaks of the pristine chitosan. The same thing observed in the incorporation of PVA in the electrolyte. PVA has O-H and C-H alkane group, in which the polymer electrolytes obtained from chitosan/PVA and chitosan/PVA with lithium showed the same spectrum pattern. The stretching vibration of N-H amine and O-H appeared as absorption peaks around 3456 cm^{-1}, 3364 cm^{-1}, and 3307 cm^{-1}. The absorption peak from C=O bond originating from deacetylated chitosan appears with weak intensity around 1585 cm^{-1}.

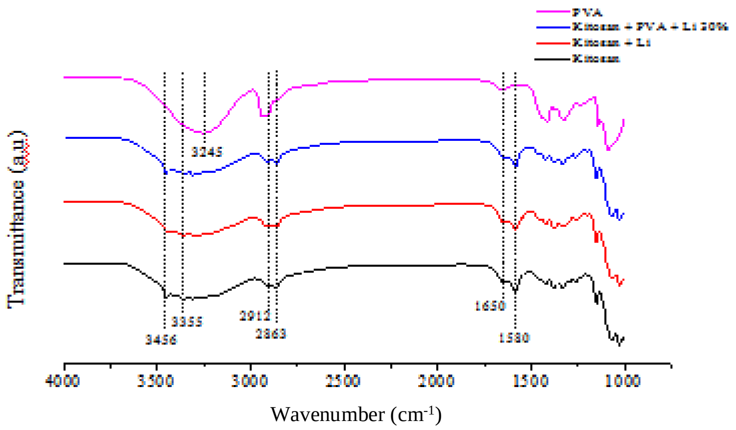

Fig. 4. ATR spectra of polymer electrolytes

Ionic Conductivity

Chitosan and PVA have low ionic conductivity. Several efforts have been involved to increase their ionic conductivity through various types of modifications: blended with other polymers, added some crosslinking agent, and synthesis of hybrid electrolytes based on organic-inorganic matter. Polymer electrolytes obtained from blending generally have better characteristics, especially the biological properties, ionic conductivity, mechanical strength, and the stability against degradation compared to the pristine polymer.

In this study, we except to obtain the best composition of chitosan, PVA, and lithium in the electrolyte which gives the best properties for the application of lithium ion battery. The optimization was carried out in two stages by varying the composition of chitosan, PVA, and $LiClO_4$. At the first stage of optimization, polymer electrolytes were synthesized by varying the amount of chitosan and PVA (85%from total weight), with fixed composition of $LiClO_4$ (15% from total weight).

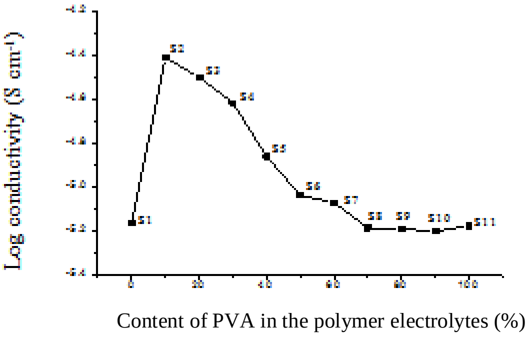

Fig. 5. Ionic conductivity of polymer electrolytes with the variation of PVA and fixed $LiClO_4$ 15%

The ionic conductivity of the polymer electrolytes is presented in Figure 5. The highest conductivity (3.89×10^{-5} S cm^{-1}) was obtained in the electrolyte with the chitosan/PVA ratio of 90/10. The second stage of optimization was carried out by varying the composition of $LiClO_4$from 20 to 40% with the fixed composition of chitosan/PVA (90/10). The ionic conductivity obtained is presented in Fig. 6. It can be clearly seen that the addition of $LiClO_4$ significantly increases the ionic conductivity. The highest ionic conductivity (4.57×10^{-3} S cm^{-1}) is given by S14, which indicates that the best composition is produced by polymer electrolyte with 70% chitosan/PVA (90:10) and 30% $LiClO_4$. The ionic conductivity is higher than the minimum standard value of ionic conductivity for lithium battery application, which is 10^{-5} S cm^{-1} [12].

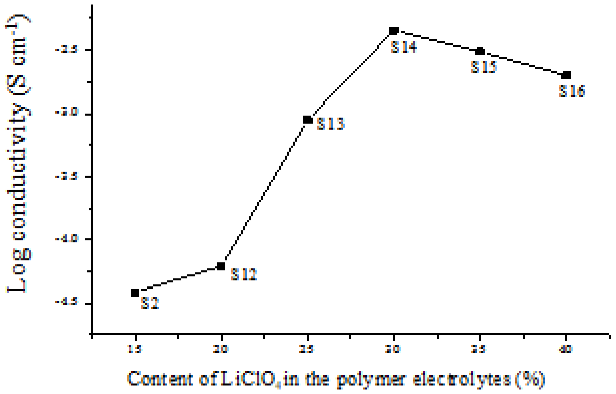

Fig.6.Ionic conductivity of polymer electrolytes with the variation of LiClO₄

Mechanical Properties

The mechanical properties of the polymer electrolytes obtained were examined through tensile test. The addition of PVA and LiClO$_4$ into chitosan clearly caused the different in the tensile strength, elongation at break, and Young Modulus, as presented in Fig. 7 and 9. It can be clearly seen that along with the increase of PVA content, the tensile strength and Young Modulus decrease, while the elongation at break increases. It might be due to the formation of hydrogen bond interactions between chitosan and PVA chains as shown in Figure 8. This interaction causes a reduction in polymer crystallinity which in turn results in the decrease of its mechanical properties.

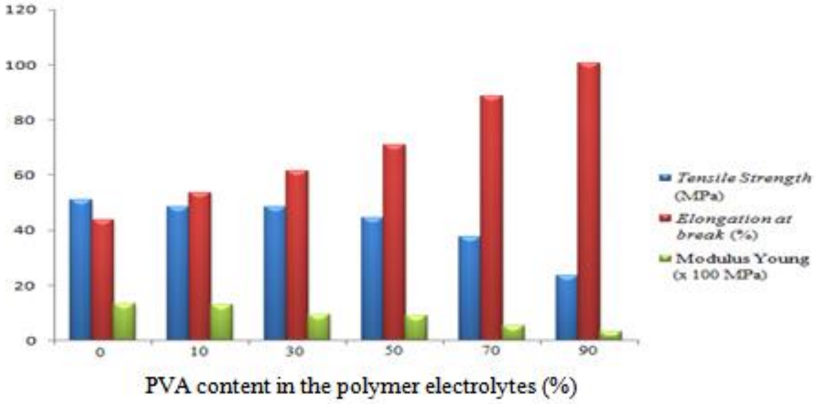

Fig. 7. The effect of PVA content to the mechanical properties of the polymer electrolytes

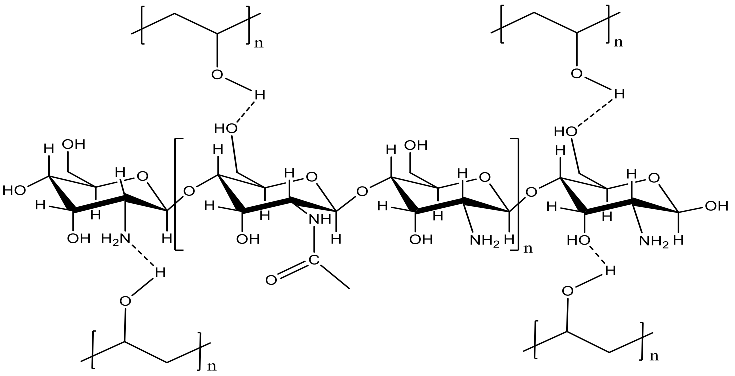

Fig. 8. The hydrogen bond interaction between chitosan and PVA chains

The same effect was also observed in the mechanical properties profile after the addition of $LiClO_4$(Fig. 9). The addition of $LiClO_4$ in the electrolyte, the tensile strength and Young Modulus decrease, while the elongation at break increases. This might also be caused by the decrease in polymer crystallinity, due to the interaction of lithium with electron-rich groups in the chitosan chain, thus disrupting the density and regularity of the chitosan chain arrangement.

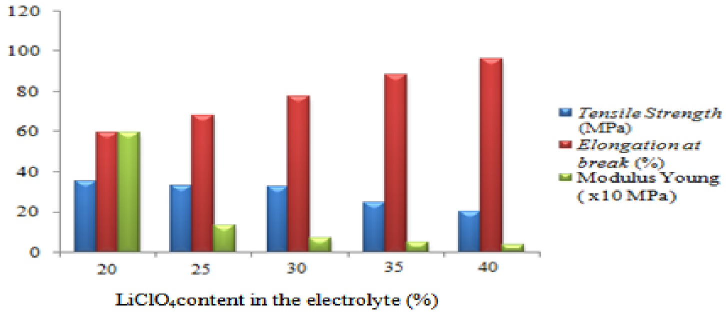

Fig. 9. The effect of $LiClO_4$ content to the mechanical properties of the polymer electrolytes

Polymer electrolyte with the highest ionic conductivity (S14) has a tensile strength of 32.24 MPa, elongation at break of 77,52%, and Young Modulus of 69.67 MPa. Although the tensile strength of S14 was not as large as the other compositions, this value has met the requirements of polymer electrolyte mechanical strength for lithium battery applications, which is greater than 30 MPa [12].

Morphology of Surface

The SEM image of pristine chitosan and chitosan-PVA blending is presented in Fig. 10a-c. Pristine chitosan has a dense structure. The addition of $LiClO_4$ resulted in the decrease of structure density. After the addition of PVA, the chitosan chain arrangement remains tenuous, and the electrolytes showed pores as a result of the interaction between chitosan and PVA chains. The cross-sectional images (Fig.10d-e) showed similar pattern between pure chitosan with and without the addition of lithium. Meanwhile, in Figure 10f, it is clearly seen that the addition of PVA and lithium simultaneously resulted in the formation of a more brittle electrolyte compared to pure chitosan, thus decreasing the mechanical properties of the blending electrolytes.

The analysis of the SEM images gives support to the ionic conductivity results and the mechanical properties of the electrolytes, in which the addition of PVA and $LiClO_4$ simultaneously caused in reduction of chitosan crystallinity, thus decreases the mechanical properties and increases the ionic conductivity. Eventually, the increase of ionic conductivity caused by the increase of both the number and the ease of lithium ion mobility due to crystallinity decrease, as well as the increase of pores to support the lithium mobility.

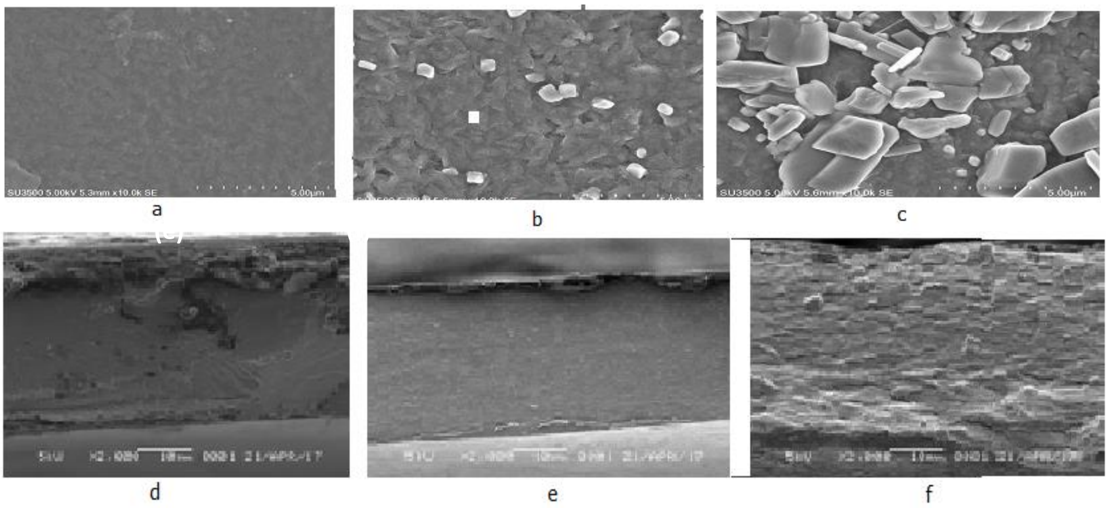

Fig. 10. SEM images of morphology: (a) chitosan; (b) chitosan with 15% $LiClO_4$; (c) chitosan/PVA 90/10 with 15% $LiClO_4$; (d) chitosan cross-section; (e) chitosan with 15% $LiClO_4$ cross-section; (f) chitosan/PVA 90/10 with 15% $LiClO_4$cross-section.

Thermal Properties

The TGA thermograms (Fig. 11) showed good stability of all the electrolytes. The mass loss below 100°C was originated from the organic solvents remain in the electrolyte. It can be clearly seen that all the electrolytes start to degrade above 225 °C. The degradation temperature of some polymer electrolytes is presented in Table 2.

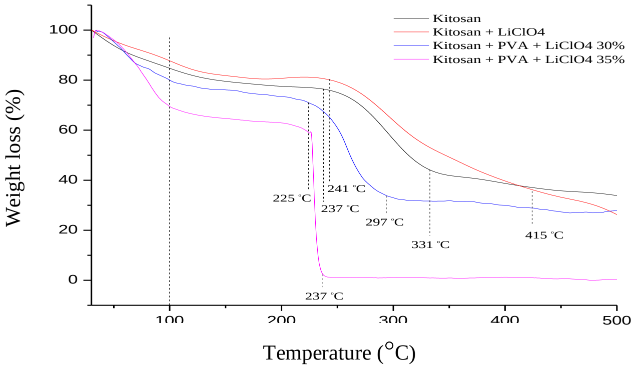

Fig. 11. TGA thermograms of polymer electrolytes

The addition of PVA and $LiClO_4$ simultaneously gave an effect on reducing the thermal stability of the polymer electrolytes. This thermal data also in line with the analysis of ionic conductivity results, mechanical properties, and SEM images discussed earlier. It can be clearly seen that the addition of 15% $LiClO_4$to chitosan matrix increases the thermal stability (Table 2). However, the increase of PVA and$LiClO_4$ content in the polymer electrolytes resulted in the decrease of its thermal stability. This might be due to the ability of a small amount of lithium salt to fill the pores on pristine chitosan, resulting in a denser arrangement of the electrolyte, thus increasing the mechanical and thermal stability. However, the excessive amount of lithium salt causes interference with pristine chitosan, due to the interaction between lithium ions and electron-rich groups in chitosan chains. This interaction makes the chitosan chain arrangement become increasingly tenuous, thereby reducing its mechanical and thermal stability. Polymer electrolyte with the highest ionic conductivity (30%$LiClO_4$) starts to degrade at around 225 °C and ended up at around 297 °C. Although the degradation temperature of this polymer electrolyte was not as large as the chitosan with and without 15% $LiClO_4$, this value has met the requirements of polymer electrolyte for lithium battery applications, which is greater than 150 °C [12].

Table 2. Degradation temperature of electrolyte polymer

Polymer electrolytes	$T_{initial}$ (°C)	T_{final} (°C)
Chitosan	237	331
Chitosan with 15% $LiClO_4$	241	415
Chitosan-PVA with 30% $LiClO_4$	225	297
Chitosan-PVA with 35% $LiClO_4$	225	237

IV. CONCLUSIONS

Synthesis of chitosan had been successfully done with the yield of 62.22% from chitin weight or 26.82% from the initial shrimp shells weight. The deacetylation degree of chitosan obtained was 77.65%. The highest ionic conductivity (4.57 x 10^{-3} S cm^{-1}) of polymer electrolytes was produced with the composition of 70% (chitosan/PVA 90/10) and 30% $LiClO_4$. The ionic conductivity increases in polymer electrolytes after blending between chitosan/PVA/$LiClO_4$compared to that the chitosan, it is due to the increase of both the number and the ease of lithium ion mobility in the electrolytes.

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