

THE EFFECT OF PLASTICIZER ADDITION TO SOLID POLYMER ELECTROLYTE BASED ON CHITOSAN MONMORILLONITE NANOCOMPOSITE

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The effects of plasticizer addition to solid polymer electrolyte based on chitosan monmorillonite nanocomposite containing lithium salt have been studied. Ethylene glycol as plasticizer is an additive with low molecular weight expected to influence intrinsic polymer properties. A plasticizer also tends to dissociate ion pairs into free cation and anion which leads to an overall enhancement conductivity. The purpose of the research is to determine optimal composition of plasticizer addition to obtain good solid polymer electrolyte. The plasticizer within the range of $0 \leq x \leq 75\%$ w/w was added into chitosan monmorillonite nanocomposite. The mixture then was casted by slow evaporation in order to obtain thick film of solid electrolyte. The sample characterizations involve ionic conductivity measurement by LCR meter, crystal structure by an X-ray Diffraction, thermal analysis by a Differential Scanning Calorimetric and mechanical properties by a Universal Testing Machine. The results show that the addition of 50% w/w plasticizer could increase the ionic conductivity from $\sim 10^{-9}$ S/cm until 2.26×10^{-4} S/cm and the polymer elasticity increase from 11.2% until 77.5% elongation break. The x-ray diffraction analysis showed that plasticizer addition make polymer more amorphous. It is concluded that the addition of plasticizer has improved the electrical and mechanical properties of the solid polymer electrolyte.

Keywords : nanocomposite, polymer electrolyte, chitosan, plasticizer

1. Introduction

Nowdays solid polymer electrolytes (SPEs) have attracted considerable attention because of their technological aspects which is widely used in energy storage components such as batteries, fuel cells, supercapacitor and a hybrid energy source [1,2]. SPEs is formed by dissolving salt in a macromolecule, typically such as poly(ethylene oxide) PEO, poly methyl metacrylate (PMMA), chitosan,

etc. The solid polymer electrolyte membrane is the key component of polymer battery that has to fulfill a series requirement, including good mechanical properties (to assure easy battery fabrication, high ionic conductivity, high lithium ion transport, wide electrochemical stability, low cost and benign chemical composition (to be environmentally friendly). Unfortunately, it is not an easy task to achieve those requirements and until now SPEs still have low ionic conductivity at ambient temperature that acts as barrier to their utility [3,4]. To overcome these problems, the realization of single ion conduction is good alternative and development of polymer nanocomposite electrolyte (PNCEs) by using layered silicate clay meets these criteria. Polymer nanocomposite electrolyte was prepared by dispersing the ceramic material such as : SiO_2 , Al_2O_3 , and clay (bentonite , monmorillonite) into a complex matrix of polymers and salts [5-8] . The idea of composite formation by dispersing the ceramic or clay materials is an attractive approach to improve stability properties by modifying (i) the local structure / morphology (ii) crystallinity degree (iii) the glass transition temperature (iv) the flexibility of the polymeric segment (v) the chemical properties of the filler particles and (vi) the interaction between heterogeneous systems of filler, salt and polymers [9].

Generally, the ionic conductivity of PNCE usually lies in the range 10^{-7} to 10^{-5} S/cm at ambient temperature. Almost all composites polymer electrolyte posses inherent obstacle which come up of their partial crystalline nature that impedes their overall ionic conductivity and in that way impose limitation on their application [3, 9-13].

In order to overcome these limitations and to increase the ionic conductivity of PNCE without affecting their stability is plasticizing the composite polymer electrolyte with small organic molecules such as ethylene carbonate (EC), propylene carbonate (PC), ethylene glycol (EG), glycerol, etc. which have high dielectric constant and low vapour pressure [14]. These plasticizers helps in improving the ionic conductivity of PNCE by (i) increasing the amorphous content of polymer electrolytes, (ii) dissociating ion pairs into free cations and anions which leads to an overall enhancement conductivity, (iii) increasing the flexibility in the polymeric segment, (iv) significant change in local structure/microstructure, (iv) lowering the glass transition temperature, T_g [9].

The plasticizer addition can increase in the ionic conductivity of 1-2 orders of magnitude and a decrease of T_g values by 40°C of plasticized polymer electrolytes samples as reported by MacFarlane et al., and Forsyth et al. [15,16]. In these works, they investigated the PEO samples plasticized with 50 wt% of propylene carbonate and 50% of dimethyl formamide. Samples of plasticized chitosan-based polymer electrolytes were also reported by Aroof et. al., and

obtained that chitosan plasticized with 50 wt% of ethylene carbonate and 10 wt% of oleic acid showed the ionic conductivity of 10^{-5} S/cm. [17,18].

In this work, new composite polymer electrolyte based on chitosan are presented. The samples of PNCEs film based on chitosan containing monmorillonite and LiClO_4 were plasticized with ethylene glycol, and the influence of this additive to the properties of PNCEs films is investigated.

2. Methodology

2.1. Materials

Chitosan (CS) from crab shells with low molecular weight used in this work was purchased from Bogor Agricultural Institute Laboratory. This chitosan was obtained by deacetylation of chitin and it had a degree deacetylation of 86%. Glacial acetic acid (HAc) obtained from Merck was used as the solvent of chitosan, monmorillonite K 10 (MMT) as a filler, and LiClO_4 as lithium salt source, both of them purchased from Sigma Aldrich and Ethylene glycol (EG) as plasticizer purchased from Merck.

2.2. Preparation of Composite

Chitosan solution was prepared by dissolving chitosan (CS) in a 1% (v/v) aqueous acetic acid solution at a concentration of 4 wt%. The mixture was stirred continuously with a magnetic stirrer until chitosan powder has completely dissolved in the acetic acid solution. Monmorillonite (MMT) was first swelled by 10% (w/v) LiClO_4 solution, then the plasticizer ethylene glycol was added with composition 10 wt%, 25 wt%, 50 wt% and 75 wt% and stirred for 1 hour. After that, each mixed solution is added to 100 ml chitosan solution and stirred for 10 hours. Then, MMT/CS/ LiClO_4 /plasticizer solution was casted on a petri dish at 50°C for 48 hours until solvent free film were obtained. The films were kept in the desiccator for further drying.

2.3. Materials Characterization

Ionic conductivity measurement were performed with a computer controlled impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) in the frequency range 42 Hz to 5 MHz.. Mechanical properties of different plasticized composite polymer electrolyte film were studied by Universal Testing Machine (UTM) strograph VGS S-E Toyoseiki based on ASTM D-1822 L. The X-ray diffraction (XRD) pattern of plasticized polymer film was recorded at room temperature using an X-ray diffractometer (Shimadzu XD-610) with Cu

K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ (Bragg angles) range $5 \leq 2\theta \leq 65$ at scan speed 3° per minute. Differential Scanning Calorimetry (DSC) studies of different plasticized polymer films were carried out with a DSC unit (Perkin Elmer).

3. Result and Discussion

3.1. Ionic Conductivity

Figure 1 shows the variation of ionic conductivity (σ_{ac}) with frequency for different concentration of ethylene glycol at room temperature for CS + 2wt.% MMT + 40 wt.% LiClO₄ + x wt.% EG. The ac conductivity patterns show a frequency independent plateau in the medium frequency region. From the graph it can be seen that the conductivity of polymer films undergo significant changes. The ionic conductivity of plasticized composite polymer film is higher than unplasticized polymer film (CS). The ionic conductivity starts increase at EG (x = 10%) until x = 50%. But at x = 75% the ionic conductivity values is not increase anymore, but tends to decrease significantly. It can be concluded that the optimum addition of plasticizer is 50 wt% for the CS/MMT/LiClO₄ composite polymer system(PNCE). Referring to previous research by Yulianti, E. et. al [19] the ionic conductivity value of unplasticized CS/MMT/LiClO₄ was $2.38 \times 10^{-5} \text{ S/cm}$ and in this work is obtained the ionic conductivity of plasticized composite polymer is $2.26 \times 10^{-4} \text{ S/cm}$ increased by 1 orde, with 50 wt.% plasticizer addition.

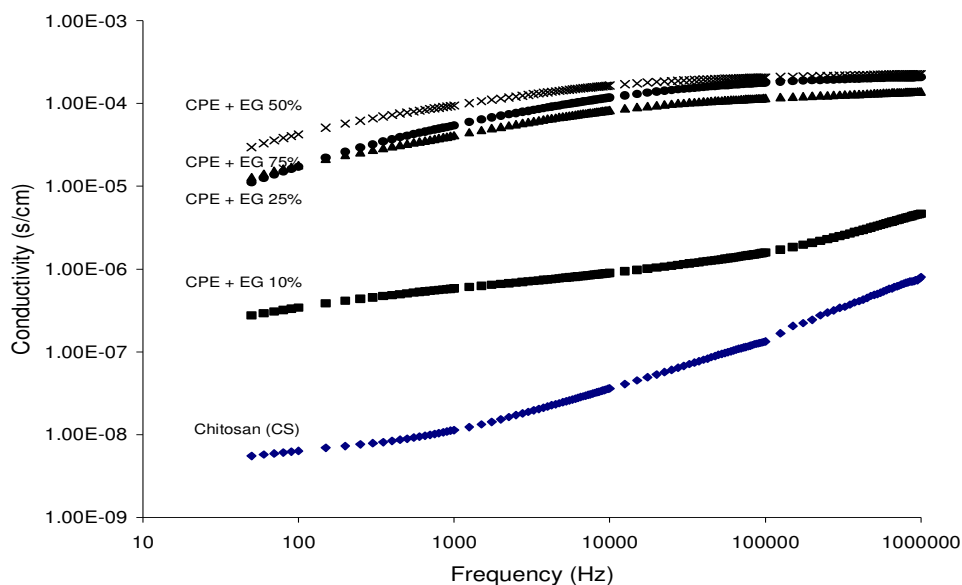


Figure 1. Variation of a.c conductivity with frequency CS + 5 wt.%MMT + 40% wt% LiClO₄ (PNCE) + x wt.% EG

Plasticizer tends to dissociate ion pairs into free anions and cations, so the amount of moving ion into the system is increased. Therefore the ionic conductivity for plasticized composite polymers were higher than unplasticized ones. Plasticizer addition also increased the flexibility of composite polymer so that ions movement in the polymer matrix become more freely [9]. The plasticizer addition also made polymer more amorphous, and this phenomena can be seen from the X-ray diffraction pattern of CS/MMT composite film in Figure 2.

3.2. X-ray diffraction

The XRD patterns for composite polymer electrolyte based on chitosan with different plasticizer concentration are shown in Figure 2. The XRD pattern has typical features namely a background hump followed by several characteristic peaks that are attributed to the host polymer (i.e., chitosan). This agrees with the result of Agnieszka et al. [9,14] and indicates that the solid polymeric films are composed of a combination of crystalline and amorphous phases. Crystalline phase is characterized by the peak at position 2θ angle of 11.97° and 18.52° , not sharp but wide peak which indicates the presence of amorphous phase. Further, the appearance of small peak at 2θ angles $\sim 27.05^\circ$ may possibly be related to the existence of SnO₂ that is contained in monmorillonite [19]. This suggests that the diffraction peaks of composite polymer electrolyte (PNCE) films are of composite nature.

The addition of ethylene glycol plasticizer brings substantial changes in the diffraction pattern of the composite polymer electrolyte with the increasing concentration of the plasticizer as observed in Fig 2(c) – (d). The main XRD peaks (due to chitosan) at 11.97° and 18.52° almost disappear and significant broadening with plasticizer addition. On the addition of ethylene glykol (EG) plasticizers up to 50% only one peak of chitosan at 18.52° is visible, whereas the addition of 75% plasticizer, the peak had disappeared and have maximum broadening, that suggest that the sample with EG = 75% has maximum disorder, shows the increasing amorphous phase in the polymer composite systems. Peak SnO₂ of monmorillonite at $\sim 27.05^\circ$ at EG = 10% and 25% is still visible, while the addition of plasticizer at 50% and 75% the peak does not appear anymore.

The addition of plasticizers into the nanocomposite polymer systems have resulted in an enhancement in the amorphous fraction in polymer film. This is due to that a plasticizer which is a small molecular weight can increase the free volume or molecular mobility of the polymer by reducing the hydrogen bonds between the polymer chains. The composition, size, and shape of the plasticizer

affects its ability to disrupt hydrogen bonding of chitosan chains. Plasticizer reduces the intermolecular force of polymer chains, therefore there is a larger space for the ions (i.e. lithium ions) to move, thereby the ionic conductivity of the PNCE system will be increase as shown in Figure 1.

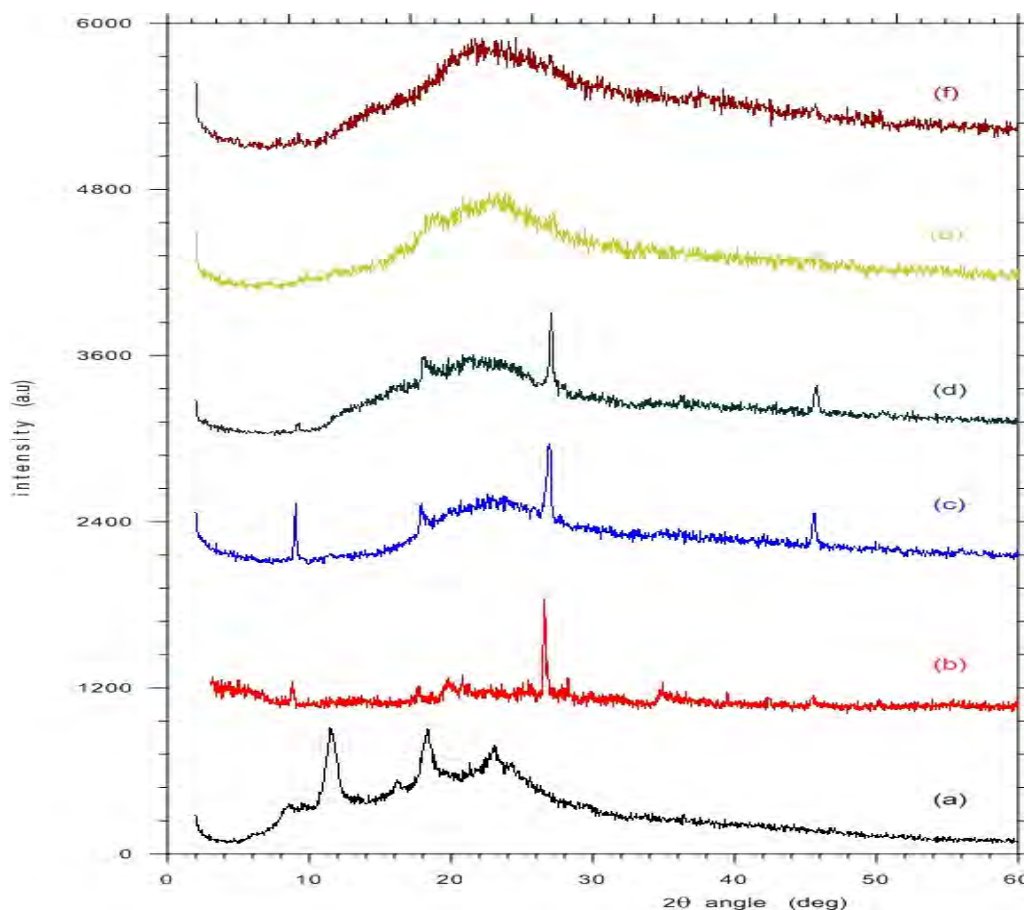


Figure 2. X-ray diffraction pattern of PNCE thin film with different concentration (x) of EG (a) chitosan, (b) monmorillonite, (c) x = 10% (d) x = 25% (e) x = 50% and (f) x = 75%.

3.3. Differential Scanning calorimetry

The thermal properties curves for of the composite polymer electrolyte (PNCE) system at various plasticizer concentrations measured by DSC are shown in Figure 3 over a wide range of temperature i.e., 30 to 450°C. In Figure 3 shows an endothermic peak which is melting temperature of PNCE crystalline fraction containing plasticizers which starts at onset temperature around 120°C. The more concentration of plasticizer added, the endothermic peaks become broader and shifted toward lower temperature and onset temperature also decreases. This is due to the addition of the plasticizer causes increasing the flexibility in the

polymeric segment, that is also convinced by the mechanical properties data of the PNCE film (i.e., the elongation break curve) that shows the PNCE films become more elastic with the higher concentration of plasticizer. These results are also consistent with measurements of X-ray diffraction pattern which shows the broadening of the peak which means higher amorphous fraction in PNCE with increasing concentration of plasticizer.

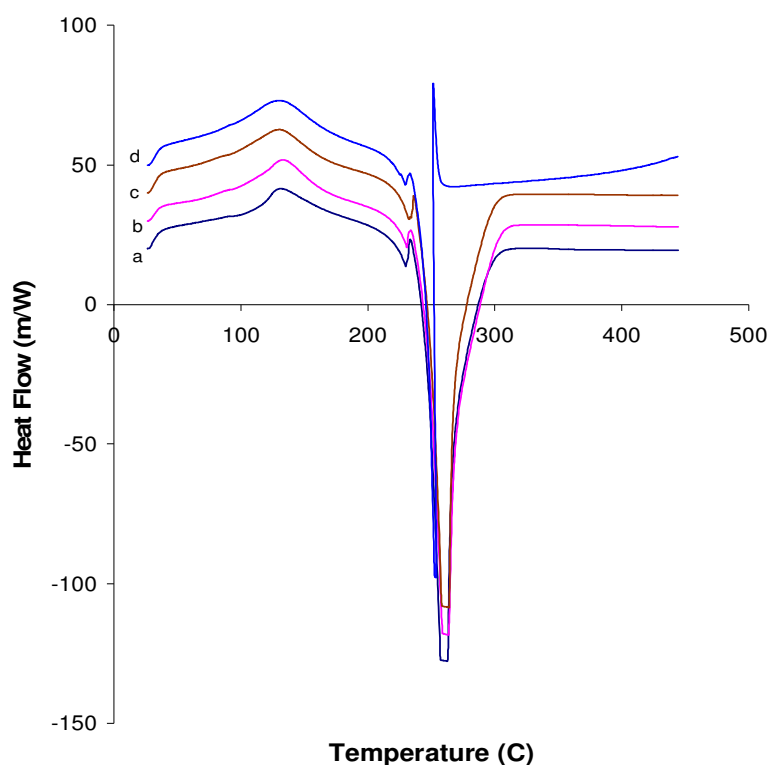


Figure 3. DSC curve of PNCE in temperature range 30 to 450°C with different concentration of EG (a) $x = 10\%$, (b) $x = 25\%$ (c) $x = 50\%$ and (d) $x = 75\%$

From the DSC curve, it is clear the effect of plasticizer addition on the thermal properties of PNCE. Further, it is revealed that that melting temperature of plasticized PNCE film decrease with increasing plasticizer concentration. Exothermic peak that appears at the onset temperature around 240 °C is a decomposition temperature of ethylene glycol. From the DSC curves it can be seen that the more concentration of ethylene glycol plasticizer is added, the exothermic peak become narrower, that means that decomposition process occurs slower. It can be concluded that PNCE films have better heat resistance and thermal properties with the increasing plasticizer concentration.

3.4. Mechanical Properties

Tensile strength and elongation break percentage were very important to explain how the mechanical characteristics of the material. Tensile strength values measured to determine the extent to which the membrane reacts to the pull force. Plasticizer is a material that can make polymer material becomes more elastic if it was added. The addition of this plasticizer is needed to overcome the stiffness properties of chitosan-based films. With the addition of the plasticizer in the polymer chains of chitosan causes inter-polymer bond can be damaged and made polymer more plasticity and flexibly. Mechanical properties data of PNCE added plasticizers ethylene glycol are shown in Figure 4 and Figure 5.

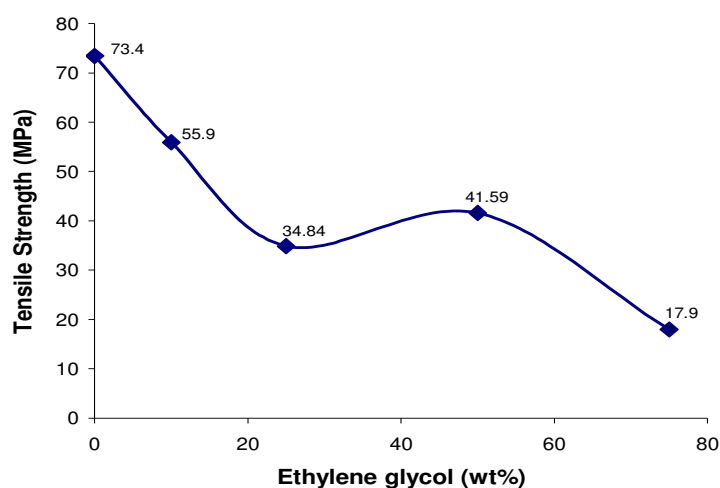


Figure 4. Tensile Strength curve of PNCE with different plasticizer concentration (x) (x = 0, 10%, 25%, 50% and 75%)

In Figure 4 it can be seen that the tensile strength of PNCE decreased with the increasing of plasticizer concentration. The unplasticized PNCE have tensile strength value 73.4 MPa, while the plasticized film with $x = 10\%$ is decreased to 55.94 MPa, and with $x = 25\%$ also decrease to 34.84 MPa. However, the plasticizer addition of 50% caused the tensile strength increased to 41.59 MPa, but at $x = 75\%$ PNCE the strength decreased again to 17.97 MPa.

Tensile measurements are usually performed in conjunction with elongation break measurement. Elongation break percentage determines the elasticity of a PNCE film. The higher the value of the elongation break, the more elastic the

PNCE film. The addition of plasticizer ethylene glycol was increase the elongation break of the PNCE films. The unplasticized PNCE film is inflexible and only has elongation break percentage 11.2%. The addition of plasticizer at composition 10 wt% has increased elongation break significantly until 60.7%, but at plasticizer concentration 25% little bit decrease to 50.7%. The highest elongation break value 77.5% is achieved at plasticizer concentration 50%. From the Figure 4 and 5 it can be seen that the optimum mechanical properties of PNCE films is achieved at plasticizer concentration of 50 wt%.

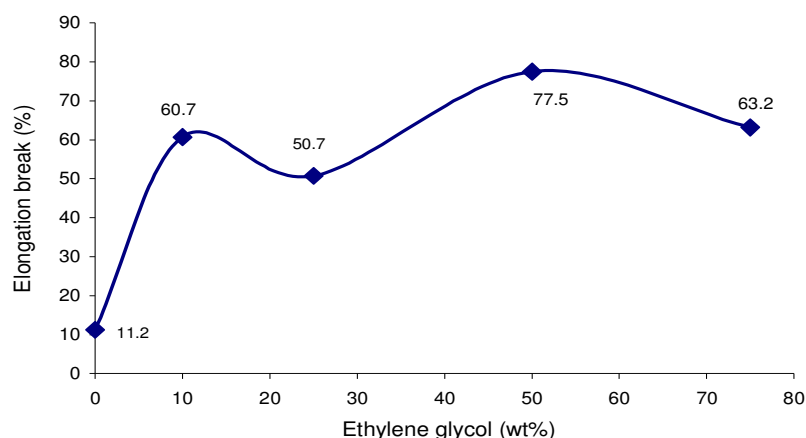


Figure 5. Elongation break curve of PNCE films with different plasticizer concentration (x) (x= 0, 10, 25, 50, and 75 wt%)

4. Conclusion

The effect of plasticizer ethylene glycol on properties of chitosan nanocomposite polymer electrolyte (PNCE) has been studied. Addition of plasticizer at concentration 50 wt% can increase the PNCE film conductivity until 2.25×10^{-4} S/cm. The plasticizer addition also influence the intrinsic properties PNCE films where the XRD pattern and thermal curves showed the PNCE films become amorphous with lower melting points. In addition to the higher plasticizer addition concentration, the PNCE films become more flexible and optimum condition is achieved at plasticizer concentration 50 wt% with elongation break 77.5%.

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