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Research paper

Preparation and characterization of Jatropha oil-based Polyurethane as non-aqueous solid polymer electrolyte for electrochemical devices

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ABSTRACT

Jatropha-oil based polyurethane is one of the initiative for replacing conventional petroleum based polyurethane. The vegetable oil-based polyurethane is more cost-effective and synthesize from renewable resources. Polyurethane was synthesized through prepolymerization method between jatropha oil-based polyol and diphenylmethane 4, 4'diisocyanate, (MDI) in inert condition. Then, lithium perchloride ion ($LiClO_4$) was added to the polyurethane system to form electrolyte film via solution casting technique. The polymer electrolytes were prepared by varying the amount of $LiClO_4$ ion 10 wt.% to 30 wt. %. The highest conductivity is achieved at 25 wt.% of $LiClO_4$ salt content, which is 1.29×10^{-4} S/cm at room temperature 30 °C. The FTIR results showed the shifting of carbonyl group (C=O) (1750 cm^{-1}–1730 cm^{-1}), ether and ester group (C-O-C) (1300 cm^{-1}–1000 cm^{-1}) and amine functional groups (N-H) (1650 cm^{-1}–1500 cm^{-1}) in polyurethane electrolytes from the blank polyurethane shows that oxygen and nitrogen atom acts as electron donor in the electrolytes system. It also confirmed that the intermolecular reaction had occurred in the electrolytes system. While, the XRD analysis showed the semi-crystalline properties of polyurethane have been reduced to amorphous phase upon the increasing addition of lithium ion. SEM results revealed the morphology analysis of the polyurethane electrolytes. There is homogenous and smooth surface in polyurethane and the dissociation of salt was observed after the addition of salt indicates there was interaction between salt and the polymer host.

1. Introduction

Polymer electrolytes are defined as solid ion conductors formed with dissolving salt in polymer having high molecular weight. Polymer electrolytes have already gaining popularity in replacing the conventional liquid electrolytes and firstly discovered in 1973 by Wright and Armand [1,2]. As the researchers managed to explore the potential of polymer electrolytes replacing the liquid electrolytes, then their attention changed to the bio-polymer electrolytes. Bio-polymer electrolytes is new types of electrolytes that have managed to gain popularity among the researchers since the green products and environmental issues has become attention worldwide. It is more biodegradable and cost effective compared to petroleum based polymer electrolytes.

Polyurethane is one of the important polymers in industries as it has a wide range of applications such as in coating industries, packaging, sealants and adhesives. Polyurethanes possess a wide range of application as mentioned above as it possess high mechanical strength, excellent abrasion resistance, high toughness and low temperature flexibility, chemical and corrosion resistance [3]. It also has a unique structure that consists of hard segment and soft segment made up from isocyanate and polyol, hence make it possess high mechanical strength and then suitable for wide range of applications [4,5]. Various synthetic PU has been reported for preparing polymer electrolyte in electrochemical devices [6–9]

In recent years, polymers developed from renewable resources, particularly plant oils have attracted much attention due to their economic, environmental, and societal advantages [10]. Jatropha oil has significant potential as a raw material for industrial applications because it is renewable and non-edible. The competitive costs of jatropha, oil compared to other oils, such as

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soybean (*Glycine max* (L.) Merr) and rapeseed (*Brassica napus* L.) [11], have attracted industrialists and academics to investigate these materials for the production of green composite polyurethane (PU). Bio-based polyurethane has been researched for many applications such as coating, adhesive, electrolyte and composite applications [3,25,12].

Based on the method of holding ions in the polymer, polymer electrolytes and bio-polymer electrolytes are divided into three forms which are solid polymer electrolytes, gel polymer electrolytes and composites polymer electrolytes [10]. Solid polymer electrolytes are in a solid form where the ions are added to the polymer so that the polymer can have conductivity characteristics. Various types of host polymer and ions are suitable prepared for solid polymer electrolytes, making it most popular compared to gel and composites polymer electrolytes. This is because the solid polymer electrolytes easier to prepare and have good properties. The host polymer that usually used for solid polymer electrolytes are polyethylene oxide [13], polyvinyl chloride [14], polymethyl methacrylate [15] and polyurethane [3,25]. It has a big potential in replacing the conventional liquid electrolytes weaknesses such as leakage, reaction with electrodes, corrosive and harmful to the environment. The polymer electrolytes can be useful in a wide range of applications. It has a wide potential to be used in electrochromic devices, solar cells, sensors and supercapacitors [16,17]. In order to have a good performance to be used in those applications, there are several criteria that should be considered in preparing a good solid polymer. For example, one of the most important elements for achieving high ionic conductivity in certain electrolytes is the chosen of the doping ions. Among the salts that researchers have been utilized and reported for lithium tetrafluoroborate (LiBF) [18], lithium perchorate ($LiClO_4$) [19], lithium bis(trifluoromethanesulfonyl) imide (LiTSFI) [20]. The ion selected must be compatible with the host polymer in order to get high ionic conductivity. In this work, the chosen of $LiClO_4$ as the doping ion is because it may possess several advantages compared to another salts such as it can be very stable at ambient moisture and less hygroscopic. Moreover, the high oxidation state of chlorine (VII) in perchlorate makes it a strong oxidant that readily reacts with most organic host polymer and exhibit high compatibility with it especially polyurethane [1,3,25].

In this research, polyurethane electrolyte was prepared from two steps of reactions starting with epoxidation reaction and follow by hydroxylation reaction. After hydroxylated polyol, reaction with isocyanate will take placed to form polyurethane in one short method. Solid polymer electrolyte was prepared with various concentration of $LiClO_4$ and polymer electrolyte achieved high ionic conductivity around 1.29×10^{-4} S/cm at room temperature 30 °C. Characterization of polyurethane to confirm their chemical structure and functionality and solid polymer electrolytes systems are studied to investigate the suitability of polymer electrolytes systems in electrochemical devices especially lithium batteries and solar cell applications.

2. Experimental

2.1. Materials

Jatropha oil (acid value of 10.5 mg KOH/g, iodine value of 97.1-111.6 g I_2/100 g) was supplied by Biofuel Bionas Sdn Bhd, Kuala Lumpur, Malaysia. Diphenylmethane 4, 4′ diisocyanate (MDI), and formic acid (98%), hydrogen peroxide (30%) and sulphuric acid (95%) were purchased from Merck, Germany. Lithium perchloride and ethylene carbonate were obtained from Sigma-Aldrich (St. Louis, USA). Methanol (99.9%) and acetone (98%), sodium bicarbonate and magnesium sulphate were supplied by System Chem AR (Kielce, Poland). All chemicals are used as received.

2.2. Synthesis of polyol

Epoxidized and hydroxylation of jatropha oil were synthesised in bulk according to slightly modified procedures that have been previously described in the literature [12]. Jatropha oil (400 g), formic acid (35.5 ml) and sulfuric (4.5 ml) were stirred continuously with mechanical stirrer for about 30 minutes at temperature 40 °C. Then, hydrogen peroxide (370 ml) was added drop by drops into the solution mixture for about 2 hours. After finish the droping H_2O_2, all the mixture was stirred continuously at 60 °C till complete reaction. The temperature was controlled not to exceed 60 °C as the high temperature will led to hydrolysis of the oxirane bond. The oxirane oxygen content was tested every one hour of reaction in accordance to ASTM D1652-97 Method A standard. After the reaction completed, the mixture of epoxidized jatropha oil was washed with distilled water with the addition of magnesium sulphate to separate the epoxidized oil and the aqueous layer. The highest degree of epoxidation was 5.1% obtained at 4 hours and 30 minutes of reactions time.

The polyol was synthesized with the mixing of methanol (180 g), distilled water (20 g) and sulphuric acid (1.2 ml) with the constant stirring for 15 minutes at 40 °C. After that, epoxidized jatropha oil (200 g) was added to mixture and the reaction was continued for another half hour at 65 °C. The produced polyol was washed with distilled water and sodium bicarbonate for three times. To make sure for no water content in polyol, the rotary evaporating process was done for 2 hr. The hydroxyl value was measured by ASTM D4274-99 Method C and the polyol of 200–220 g/KOH hydroxyl value was obtained. The sample was kept with $MgSO_4$ drying agent and inert condition.

2.3. Synthesis of polyurethane

The jatropha oil-based polyurethane was synthesized in a 250 ml four neck round bottom flask equipped with a thermometer, condenser and mechanical stirrer incorporating a nitrogen gas inlet. 50 ml of polyol was mixed with calculated amount of diphenylmethane 2′4 diisocyanate (MDI). The reaction mixture was set around 70 °C. When the heat was stable for around 5–10 minutes, MDI was added drop by drop into the polyol for about one hour. The raction was continue to have one hour and reaction temperature was increased by 80 °C. After the reaction was complete, the reaction mixture was cooled down to 40 °C.The polymer was stored in sealed glass bottles with nitrogen gas inlet. The urethane linkage was expected to form as the result of the complete reaction between the polyol and isocyanate and the reaction scheme as shown in Scheme 1. PU synthesized sample was sent for further characterization.

2.4. Preparation of PU solid polymer electrolyte

Fig. 1 schematically represents the preparation process of PU and LiClO4 with EC. The preparation of PU solid polymer electrolyte was prepared as follows: Firstly, the calculated amount of lithium perchlorate ($LiClO_4$) range of 10–30 wt % was mixed with ethylene carbonate (EC) (20 wt %) with the addition of 3 ml acetone as solvent. The mixture was stirred in 50 ml sealed beaker at room temperature for 12 hr, and the uniform suspension was obtained; secondly, the suspension was added into the polyurethane with the present of acetone as solvent in nitrogen gas condition. The reaction was stirred for 2 hours at the room temperature; thirdly, after completion of the reaction, the polymer salt was poured into the Teflon mould and was kept into desecrator for drying process for one day; finally, dry film solid polymer electrolyte was obtained and keeps in desecrator for further testing. Formulation of PU with $LiClO_4$ and EC content was listed at Table 1.