UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF JATROPHA OIL-BASED POLYURETHANE ACRYLATE POLYMER ELECTROLYTE

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By

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Solid polymer electrolyte has been extensively studied as an alternative to liquid electrolyte which is often affected by several issues including leakage, deformation and limited range of operating temperature. Bio-based polymer derived from vegetable oil has been proposed to substitute petroleum-based polymer due to its fluctuations in price, non-renewable resources and non-environmentally friendly. A non-edible jatropha oil (JO), processed from seeds of *Jatrophacurcas,*has received much attention due to its high-quality bio-fuel. The present study was conducted in an attempt to synthesize polyurethane acrylate (PUA) as host polymer from JO and to evaluate polymer performance supplemented with Li salt and plasticizers as polymer electrolytes. In the study, bio-based polyol was synthesized by epoxidation and ring opening reactions. Toluene 2, 4-diisocyanate (TDI) was added to polyol followed by hydroxylethylmethylacrylate (HEMA) to produce PUA. Hexanedioldiacrylate (HDDA) was used as a cross-linkable active diluent and Darocur 1173 (D-1173) was used as photoinitiator in UV curable PUA films. Lithium perchlorate ($LiClO_4$) salt, varying from 5 wt% to 30 wt%, was used in PUA electrolyte to determine the optimum ionic conductivity. PUA with 25 wt% lithium salt recorded the highest conductivity of 6.4 x 10^{-5} Scm^{-1}. The cation transference number achieved was 0.99, whereas the electrochemical stability exhibited 4.0 V. The spectroscopy analysis examined by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy showed the interaction of lithium salts with oxygen and nitrogen atom in PUA polymer. The glass transition temperature of PUA electrolyte was lower than pristine PUA and they were negligible with increase in Li salt in the polymer electrolyte. The melting temperature of PUA electrolyte did not show significant trend with Li salt supplementation. The crystallinity and morphology studied showed that the polymer electrolyte was amorphous with the addition of salt which confirmed that the mixtures were homogeneous. The best of 25 wt% lithium salt was chosen to further study on the effect of plasticizers on the ratio of 3 wt% to 15 wt% ethylene carbonate (EC) in PUA electrolyte. The 9 wt% of EC showed the ionic conductivity had improved to 7.86 x10^{-4} Scm^{-1}. The inclusion of plasticizers did not show any interaction changes in the polymer electrolyte by FTIR and NMR. The glass transition temperature and melting temperature decreased with the addition of plasticizers. Further examination on the crystallinity and morphology showed that the salt was not homogeneously distributed over polymer matrix when the polymer exhibited a semi-crystalline phase. Study on the electrochemical stability of polymer electrolyte widened to 4.0V. The bio-based polyurethane acrylate JO exhibited a high ionic conductivity and electrochemical stability that have potential applications for electrochemical devices. However, the incorporation of plasticizers did not show any significant improvement on thermal properties observed in the study.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN POLIMER ELEKTROLIT POLIURETANA AKRILAT BERASASKAN MINYAK JARAK

Oleh

TUAN SYARIFAH ROSSYIDAH BINTI TUAN NAIWI

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Elektrolit polimer pepejal telah banyak dikaji sebagai alternative kepada elektrolit polimer cecair yang sering mengalami beberapa isu termasuklah kebocoran, perubahan bentuk dan mempunyai suhu operasi yang terhad. Polimer bio terbitan minyak sayuran telah disarankan untuk mengganti polimer berasaskan petroleum oleh kerana ketidaktentuan harga, sumber yang tidak boleh dipulih kembali dan tidak mesra alam. Minyak jatropha (JO) yang tidak boleh dimakan, yang diproses daripada biji benih Jatropha curcas, telah banyak mendapat perhatian kerana kualiti bahan bakar yang tinggi. Kajian ini dijalankan dalam satu usaha untuk mensistesis poliurethana akrilat (PUA) daripada minyak jarak sebagai polimer utama dan menilai prestasi JO polimer yang ditambah dengan garam litium dan pemplastik sebagai elektrolit polimer. Dalam kajian ini, poliol berasaskan bio telah disintesis melalui pengepoksidaan dan reaksi pembukaan cincin oxiran. Toluena 2,4-diisosianat (TDI) telah ditambahkan kepada poliol diikuti dengan hidroksiletilmitilakrilik (HEMA) untuk menghasilkan PUA. Heksandioldiakrilat (HDDA) telah digunakan sebagai pelarut aktifsilang dan Darocur 1173 (D-1173) digunakan sebagai pemula pempolimeran filem PUA di bawah sinaran ultra ungu (UV). Garam litium perklorat ($LiClO_4$) dengan peratus berat yang berbeza dari 5 % ke 30 % telah digunakan dalam penyedian elektrolit PUA untuk mencari kekonduksian ionik yang optimum. PUA dengan 25 % garam litium mempunyai kekonduksian yang tertinggi 6.4 x 10^{-5} Scm^{-1}. Nombor transfer kation yang tercapai ialah 0.99 manakala kestabilan elektrokimia mencapai 0.4 V. Analisis spektroskopi melalui spektroskopi infra-merah Fourier (FTIR) dan resonan magnet nuklear (NMR) menunjukkan interaksi garam litium dengan atom oksigen dan nitrogen dalam polimer PUA. Suhu peralihan kaca elekrolit PUA adalah lebih rendah daripada PUA dan diabaikan dengan peningkatan garam litium dalam elektrolit polimer. Suhu lebur elektrolit PUA tidak menunjukkan trend yang ketara dengan penambahan garam litium. Kajian penghabluran dan morfologi menunjukkan bahawa elektrolit polimer adalah amorfus dengan pertambahan garam mengesahkan bahawa campuran adalah homogen. Sebanyak 25 %

garam lithium telah dipilih untuk kajian lanjut atas kesan pemplastik dalam nisbah 3 % ke 15 % etilenakarbonat (EC) dalam elektrolit PUA. Kadar 9 %EC menunjukkan bahawa kekonduksian ionic telah meningkat kepada 7.86 x10^{-4} Scm^{-1}. Penambahan bahan pemplastik tidak menunjukkan sebarang perubahan interaksi dalam elektrolit polimer oleh analisis FTIR and NMR. Suhu peralihan kaca dan suhu lebur menurun dengan penambahan bahan pemplastik. Kajian penghabluran dan morfologi menunjukkan bahawa garam tidak diedarkan secara homogeny dalam matriks polimer apabila mempamerkan fasa separa kristal. Kajian stabilan elektrokimia elektrolit polimer didapati melebar kepada 4.0V. Minyak jarak poliurethana akrilat berasaskan bio menunujukkan kekonduksian ionik yang tinggi dan kestabilan elektrokimia berpotensi untuk aplikasi peranti elektrokimia. Walaubagaimanapun, penggabungan pemplastik tidak memperlihatkan penambahbaikan yang ketara pada sifat terma dalam kajian ini.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
DC	Direct current
DMF	N, N-dimethylformamide
DSC	Differential Scanning Calorimeter
DTG	Differential Thermal Gravimetry
EC	Ethylene carbonate
EJO	Epoxidizedjatropha oil
FA	Fatty acid
FTIR	Fourier Transfrom Infrared
HDDA	Hexanedioldiacrylate
HEMA	Hydroxylethylmethylacrylate
$LiClO_4$	Lithium perchlorate
LSV	Linear sweep voltammetry
MDI	2,4-diphenylmethane diisocyanate
MG49	49% poly(methyl methacrylate) grafted natural rubber
NMR	Nuclear Magnetic Resonance
OHv	Hydroxyl value
OOC	Oxirane oxygen content
PAA	Poly(acrylic acid)
PEG	Poly(ethylene glycol)
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
P(GMA-co-MMA)	Polygylcidyl methacrylate-co-polymethyl methacrylate
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
PU	Polyurethane
PUA	Polyurethane acrylate
SEM	Scanning Electron Microscopy
SiO_2	Silicon dioxide
TDI	Toluene 2,4-Diisocyanate
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
T_m	Melting point temperature
UV	Ultraviolet
XRD	X-Ray Diffraction analysis

CHAPTER 1

INTRODUCTION

1.1 Introduction to bio-based polymer electrolyte

Solid polymer electrolytes have received wide attention on applications for electrochemical devices such as rechargeable batteries, photoelectrochemical cell, supercapacitor and electrochemical devices (Su'ait *et al.*, 2014). It is an alternative to the present liquid electrolytes that suffers from leakage, narrow range of operation temperature, deformation and explosion upon heating whereas solid polymer electrolyte promises good safety, high stability, and simple fabrication application. However, the solid polymer electrolyte suffered from low ionic conductivity compared to the liquid electrolyte. Many modifications have been studying by researchers to improve the property of polymer electrolyte including mechanical, electrochemical and thermal stability (Wong *et al.*, 2014).

An earlier study used polypropylene, polysulfone, poly(tetrafluoroethylene) and polyethylene oxide as host polymer electrolyte (Florjańczyk *et al.*, 2014). Those synthetic polymers are petroleum based polymers. A recent study is more focused on developing bio-based polymers because of the environmental issues, fluctuation prices of petroleum and nonrenewable resources. Bio-based polymer possesses advantages such as environmental friendly, low-cost, abundance and sustainable. The polymer obtained from renewable resources such as the natural polymer or vegetable oils like soybean oil, linseed oil, and palm oil have attracted attention in recent works because the functionalization of triglycerides of fatty acid in oil can undergo modification.

Biopolymer electrolyte from the natural polymer such as cellulose and chitosan have studied rapidly compared to the bio-based polymer that are rarely reported (Ma and Sahai, 2013; Rudhziah *et al.*, 2015). Triglycerides of vegetable oils consist of unsaturated carbon bonds that can be functionalized and be used as a starting material to produce polymers (Su'ait *et al.*, 2014). Of late, there has a lot of research which concerns the production of green polymers. There are some studies concerning synthesizing polyurethane from polyol which are obtained from vegetable oil.

1.2 Polyurethane acrylate as polymer electrolyte

Polyurethane is one of the polymers used in solid polymer electrolyte due to its high thermal, chemical stability, good mechanical strength, high elasticity and simple preparation process. Besides, it has good miscibility between lithium ion to enhance the ion transport in the polymer electrolyte (Wong *et al.*, 2014). The low glass transition temperature (T_g) and higher segmental motion of polyurethane can lead to a higher mobility of the dissolved ions. Polyurethane end-caped with the acrylate group exhibited a wide range of mechanical and electrical properties and showed a good compatibility with lithium electrodes depending on the different composition and acrylate used.

Polyurethane acrylate (PUA) is a copolymer that consists of urethane linkage (-NHCOO-) and the acrylate groups in its molecular structure. It was synthesized from polyol and isocyanate with the addition of acrylate compound(Digar *et al.*, 2002). Commonly, the PUA has synthesized from polyether or polyester polyol of synthetic polymer since there have reactive sites to react with the isocyanate group. The properties of vegetable oil that can be modified to polyol have been studying to produce bio based polymers.

The previous study has synthesized polyurethane from polyester or polyether group but mostly from polyethylene glycol. Most of the polyurethane are applicable for coating purposes. However, polyurethane has low chemical resistance, high viscosity, and low physical properties. Then, the prepolymer of urethane acrylate is synthesized with an excess of isocyanate group and end capping by the acrylate group. A small amount of reactive diluent has employed to prepolymer in order to control the viscosity of the prepolymer. Urethane acrylate mostly applicable to coating purposes of in situ polymerisation via UV curable in the presence of reactive diluent and free radical photoinitiator.

Urethane acrylate as oligomer has studied basically for UV curable polymers. Most of the studies on acrylate polymers are related to the UV radiation preparation method that has very high speeds of curing that leads to high productivity, lower energy consumption, reduction of volatile organic compounds emission, reducing risk of fires, improving aspects of occupational safety and health and so forth (Barbeau *et al.*, 2000: Asif *et al*., 2004). Otherwise, monomer derived from vegetable oil are environmentally friendly and are low cost compared to the synthetic polymer from petroleum.

Jatropha oil has attention to modify to bio based polymers. The study on jatropha oil polyurethane as host polymer electrolyte has reported (Mustafa., 2016). Polyurethane acrylate synthesized from jatropha oil have also studied for coating purpose (Ariffin., 2017). In this study, bio-based polyol is derived from jatropha oil to synthesize the bio-based polyurethane acrylate polymer and to study polyurethane acrylate as based polymer electrolyte. Jatropha oil is anon-edible oil which contains 78.9% unsaturated fatty acids consisting mainly of oleic acid and linoleic acid which is a promising candidate for chemical purposes. This high degree of fatty acid can undergo chemical modification to produce polymers with desired properties. PUA polymer is used in the preparation of polymer electrolyte. The effect of different percentage of lithium salt and ethylene carbonate to ionic conductivity and electrochemical stability have studied as well as chemical interaction, thermal and morphology of polymer electrolyte films.

1.3 Problem statement

The commercial polyurethane acrylate is produced from petrochemical-based polyol with an excess of isocyanate. The fluctuation of petroleum, environmental issue and the sustainability of synthetic polymer problems, vegetable oil-based have attention as an alternative for producing bio-based polyol. Therefore, bio-based polyol synthesis of jatropha oil may replace the dependency on petroleum based polymers in order to overcome the petroleum resource depleting and environment issue.

The conventional liquid electrolyte has problems such as leakage, tendency to explode and can be deformed upon heating. Solid polymer electrolyte is to overcome the liquid electrolyte problems. However, solid polymer electrolyte suffers from poor ionic conductivity. The solid polymer electrolyte should consist of moving anion and cation enhancing by salt and plasticizer to obtain high ionic conductivity. Due to the limited study on synthesized of polyurethane acrylate from jatropha oil polyol, this study may contribute to production of high performance polymer electrolyte with high ionic conductivity and electrochemical stability.

1.4 Objectives of study

The main objective of this project is to study the potential for jatropha oil as a bio-based polymer for solid polymer electrolyte. Polyurethane acrylate jatropha oil based polymers has synthesized and characterized. The specific objectives are listed in order to achieve the main objective which are:

1. To prepare polyurethane acrylate jatropha oil as a bio-based polymer.
2. To obtain UV curable polyurethane acrylate jatropha oil electrolyte films.
3. To identify the electrochemical, chemical and thermal properties of the bio-based polymer of polyurethane acrylate electrolyte.

1.5 Scope of study

The scope of this study can be expressed as follows.

1. Preparation of bio-based polyol of jatropha oil is done by epoxidation and oxirane ring opening reaction. The chemical properties of epoxy jatropha oil (EJO) and obtaining polyol were investigated. Polyurethane

acrylate was prepared by addition of isocyanate and acrylate group to the bio-based polyol.

2. Bio-based PUA polymer electrolyte was prepared by varying the addition of lithium salt from 5-30wt%. The optimum conductivity achieved by polymer electrolyte was selected to prepare the polymer electrolyte with different percentage of plasticizer. The PUA polymer electrolyte film was prepared by the solution casting method of UV curing.
3. The electrochemical, chemical and thermal properties of the polymer electrolyte films were investigated.

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PUBLICATION

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