UNIVERSITI PUTRA MALAYSIA

MICRO AND NANOCRYSTALLINE CELLULOSE FIBRE-REINFORCED JATROPHA OIL-BASED POLYURETHANE COMPOSITE FILMS

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By

SYEED SAIFULAZRY OSMAN AL EDRUS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

November 2017

This thesis dedicated to my beloved parent, siblings, supervisor; Prof Dr Luqman Chuah and mentor; Prof Dr Paridah Md Tahir.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor Philosophy

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Chair: Professor Luqman Chuah Abdullah, PhD
Faculty: Institute of Tropical Forestry and Forest Products

One of the major drawbacks of using neat bio-based polymer is its poor mechanical properties. Since ancient, cellulose fibres always become preferable reinforced material to enhance mechanical properties esspecially for composite products. Number of studies on polyurethane and polyol from jatropha oil for various applications have been carried out, but none of it incorporating cellulose fibre as a reinforcement material. In this study, composite films from jatropha oil-based polyurethane (JOPU) reinforced with microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) fibres were prepared using film casting method. JOPU was produced by reacting jathropha oil polyol and reacts with 4,4'-diphenyl-methane diisocyanate (MDI). Dimethylformamide (DMF) was used as solvent to disperse MCC and NCC fibres prior to mixing with JOPU. Different fibre loadings ranging from 2.5 to 10 wt. % for MCC, and 0.10 to 1.50 wt. % for NCC were used.

The average size of MCC and NCC used in this study were 112.3 µm and 180.82 nm for length and 21.4 µm and 11.29 nm in diameter respectively. Thermogravimetric analysis shows that NCC has lower thermal stability than MCC. The crystallinity index (CI) of cellulose was decreased from 85.3% in the form of MCC to 78.0% after being reduced to NCC. Composite films made from JOPU/MCC and JOPU/NCC mixtures were successfully produced. The addition of MCC was not affected the colour but had increased density, reduced transparency and roughened surface morphology of JOPU/MCC films. In contrast with for JOPU/NCC films, only the colour of the films was affected changing from bright golden-yellowish to darker golden-yellowish colour. Effects on other properties were marginal. FTIR spectroscopy shows typical polyurethane spectra for all films indicate addition of MCC and NCC not affect much on chemical properties of the films. The thermal stability of JOPU film (T_g, 5.05 °C) was found reduced with addition of fibres with T_g range of 3.72 to -2.31 °C for JOPU/MCC films and 2.14 to -0.97 °C for JOPU/NCC films. The tensile strength for JOPU/MCC and JOPU/NCC films were increased from 54 to 356 % and 132 to 229 % respectively. For tensile modulus, increment were recorded from 49 to 2366 % and 173 to 653 %, respectively. In contrast, elongation at break appears to be dramatically declined from 340 % for JOPU to as low as 54 % in JOPU/MCC films and 124 % in JOPU/NCC films.

Both water wettability and water uptake properties found increased as the content of MCC and NCC increased. Rapid wettability was recorded in less than 10 sec. esspecially in JOPU/NCC films. However the water uptake after 5 days soaking shows plateau trend at 3 to 5% for JOPU/NCC films compared to JOPU/MCC films which shows increasing trend 4 to 16 %.

As overall conclusion, the addition of cellulose fibres (esspecially NCC) even at low amount in JOPU-based films had succesfully enhanced mechanical properties; tensile strength and modulus, and shows minimal effects on physical properties of the films. However, other properties; thermal stability, elongation at break, water wetabillity and water uptake, found significantly affected.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

FILEM KOMPOSIT POLIURETANA BERASASKAN MINYAK JATROPHA DIPERKUKUH GENTIAN MIKRO DAN NANOKRISTALIN SELULOSA

Oleh

SYEED SAIFULAZRY OSMAN AL EDRUS

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Salah satu kelemahan utama menggunakan polimer berasaskan bio adalah sifat mekanikalnya yang lemah. Sejak dari dulu, gentian selulosa sentiasa menjadi bahan memperkukuh untuk meningkatkan sifat-sifat mekanik untuk produk komposit. Terdapat beberapa kajian mengenai poliol dan poliuretana dari minyak jatropha telah dijalankan untuk pelbagai aplikasi. Walau bagaimanapun, tidak ada kajian penghasilan filem komposit dengan menggabungkan gentian selulosa sebagai bahan pengukuh dalam matriks poliuretana (JOPU) berasaskan minyak jatropha. Dalam kajian ini, filem komposit dari JOPU diperkukuh dengan selulosa mikrokristalin (MCC) dan gentian selulosa nanokristalin (NCC) telah disediakan menggunakan kaedah *casting* filem. JOPU dihasilkan dengan reaksi tindak balas poliol minyak jathropha dengan 4, 4 '-depenil-metana diisosianat (MDI). Dimetilformamid (DMF) digunakan sebagai pelarut untuk menyebarkan gentian MCC dan NCC sebelum dicampur dengan JOPU. Kandungan gentian yang berbeza digunakan antara 2.5 hingga 10 % berat bagi MCC, dan 0.10 hingga 1.50 % berat bagi NCC.

Saiz purata MCC dan NCC yang digunakan dalam kajian ini masing-masing mempunyai panjang 112.3 μm dan 180.82 nm serta diameter 21.4 μm dan 11.29 nm Analisis thermogravimetrik menunjukkan bahawa NCC mempunyai kestabilan haba yang lebih rendah berbanding MCC. Indeks kristal (CI) selulosa menurun dari 85.3% dalam bentuk MCC hingga 78.0% selepas menjadi NCC. Filem komposit yang dihasilkan daripada campuran JOPU/MCC dan JOPU/NCC telah berjaya dihasilkan. Penambahan MCC tidak menjejaskan warna tetapi telah meningkatkan ketumpatan, mengurangkan ketelusan dan morfologi permukaan filem JOPU/MCC. Sebaliknya, untuk filem JOPU/NCC, hanya warna filem yang terjejas dengan berubah dari warna cerah kuning cerah keemasan ke warna kuning gelap keemasan. Kesan ke atas sifat-sifat lain adalah kecil. Spektroskopi FTIR menunjukkan spektrum poliuretana biasa untuk semua filem menunjukkan penambahan MCC dan NCC tidak menjejaskan banyak sifat kimia filem. Kestabilan haba filem JOPU (T_g, 5.05 ° C) didapati menurun dengan penambahan gentian dengan julat T_g sebanyak 3.72 hingga -2.31 ° C untuk filem JOPU/MCC dan 2.14 hingga -0.97 ° C untuk filem JOPU/NCC. Kekuatan tegangan untuk filem

JOPU/MCC dan JOPU/NCC telah meningkat masing-masing dari 54 kepada 356% dan 132 kepada 229%. Bagi modulus tegangan, kenaikan telah direkodkan masing-masing dari 49 kepada 2366% dan 173 kepada 653%. Sebaliknya, pemanjangan pada rehat kelihatan menurun secara dramatik daripada 340% untuk JOPU sehingga serendah 54% dalam filem JOPU/MCC dan 124% dalam filem JOPU/NCC. Kedua-dua sifat kebolehbasahan air dan sifat pengambilan air meningkat apabila kandungan MCC dan NCC bertambah. Kebolehbasahan yang cepat dicatatkan dalam masa kurang dari 10 saat terutamanya dalam filem JOPU/NCC. Walau bagaimanapun pengambilan air selepas 5 hari rendaman menunjukkan trend mendatar antara 3 hingga 5 % untuk filem JOPU/NCC berbanding filem JOPU/MCC yang menunjukkan trend peningkatan 4 hingga 16 %.

Sebagai kesimpulan keseluruhan, penambahan gentian selulosa dalam filem berasaskan JOPU mempunyai kesan minima pada sifat-sifat fizikal tetapi sangat meningkatkan kekuatan dan modulus tegangan (terutamanya NCC) walaupun pada kandungan yang sedikit. Walau bagaimanapun, sifat-sifat lain; kestabilan haba, pemanjangan pada rehat, air basah dan pengambilan air, didapati banyak terjejas.

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I am also would like to take this opportunity to acknowledge Universiti Putra Malaysia for providing me scholarship and study leave to pursue my PhD.

I certify that a Thesis Examination Committee has met on 14 November 2017 to conduct the final examination of Syeed SaifulAzry Osman Al Edrus on his thesis entitled "Micro and Nanocrsytalline Cellulose Fibre-Reinforced Jatropha Oil-Based Polyurethane Composite Films" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Doctor of Philosophy

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LIST OF ABBREVIATIONS

CI	Crystallinity Index
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
DTG	Derivative Thermogravimetric
EJO	Epoxidized jatropha oil
FESEM	Field-Emission Scanning ElectronMicroscopy
FTIR	Fourier Transform Infra Red
INTROP	Institute of Tropical Forestry and Forest Product
JOPU	Jatropha oil-based polyurethane
MCC	Microcrystalline cellulose
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated celulose
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer
TEM	Transmission Electron Micrograph
UPM	Universiti Putra Malaysia
WXRD	Wide angle X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction of study

For a century, mankinds have rely so much on petro-chemicals and gained very much benefits from it. Petro-chemicals occupied 80% of polymer market and has been exploits in numerous ways include generating energy, raw material for industries, intermediate and derivatives products and also household products (Iman and Maji, 2015). The dependence of human on petro-chemicals has leads various complications to environment and ecosystem due to its intrinsic properties that mostly non-biodegradable and contain toxic substances. In addition, with the issues on price fluctuation and depleting supply of petroleum oil, it is crucial to find substitute materials to minimize reliance on petro-chemicals polymers (Tenorio-Alfonso et al., 2017). Biorenewable polymers derives from biomass are possible alternative to petro-chemicals polymers. The estimation of the total investment in the biomass sector from 2008 to 2021 is nearly $104 billion (Jawaid et al. 2017). Plant-based biomass is the largest natural resources and abundantly available worldwide. In general, biorenewable polymers derives from biomass divided into three main types; (1) polymers directly synthesized from plant-based biomass, (2) polymers synthesized from bio-based monomers and (3) polymers produces from naturally or genetically modified organism/animal.Figure 1.1 summarize general types of biorenewable polymers sources.

In malaysia, around 168 million tons of plant-based biomass was produced annually from it natural forest and commercial plantation (Ozturk et al., 2017). Numbers of commodities been planted as a commercial crop for instance oil palm, rubberwood, kenaf and jatropha. Among those, for 2016, industries driven by oil palm and wood-based products are the most contribute to the country income with values approximately RM 64.6 billion and RM 22.1 billion, respectively (MPOB 2017; MTIB, 2017). For oil palm alone, it constitutes more than 90% of the country total biomass (Loh, 2017) and planted in 5.74 million ha of land (MPOB, 2017). Due to plant-based biomass industries in Malaysia are focusing on production of timber, oil and rubber latex, thus polysacharides (i.e. cellulosic fibres) and lipid/oil (i.e. tryglycerides) polymers are widely available and ready to be exploits into diversify products.

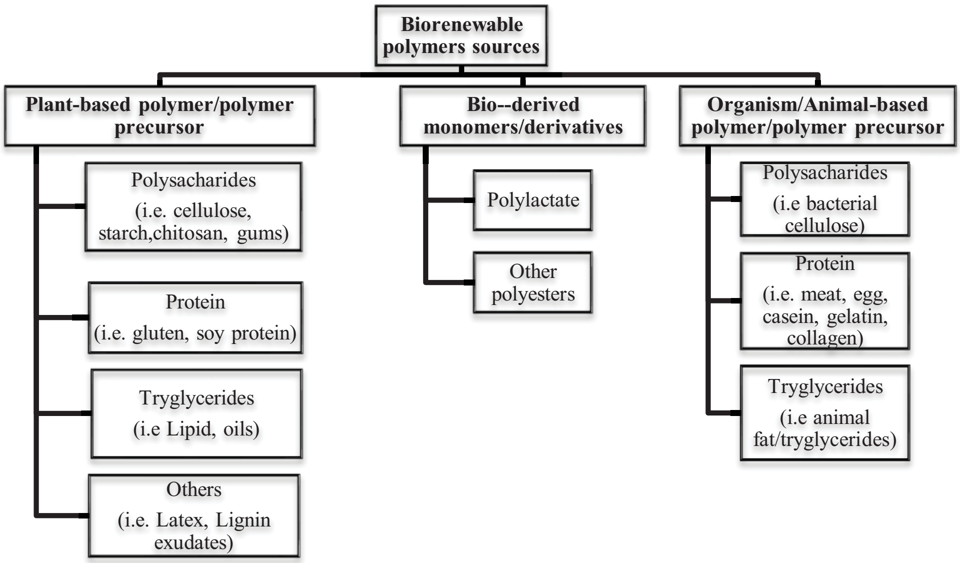

Figure 1.1: General types of biorenewable polymers sources
(Adapted from Thakur and Thakur, 2016)

1.1.1 Cellulose as composite reinforcement material

Since ancient, cellulosic fibres have been used for reinforced materials due to it huge availability resources and it natural function as a structural and reinforcement component for plant/trees. It has been used for composite reinforcement materials for many products that available today, especially for construction, furniture, automotive, building component etc. However, after the synthetic fibres, such as fibre glass, carbon fibres, plastic filament etc have dominant the market, the cellulosic fibres only been used for specific products of which could not been replaced by those synthetic fibres due to certain reasons such as economical aspect, aesthetic values and inherent properties. As mentioned earlier, Malaysia generates huge amount of cellulosic materials as a by-product from it major industrial commodities such as oil palm. By exploiting these resources, it is not only able to abate the disposal problem and resolve the environmental issues caused by synthetic fibres but it also creates value-added products from renewable resources.

The utilization of cellulose as reinforcement materials can be in original form or micro and nano-size fibres. Conventionally, the original form (i.e. solid timber) and micro size fibres such as pulverized fibre, wood pulp and microcrystalline cellulose (MCC) are widely used due to readily available in the market. However, few drawbacks are always associate with using cellulose as composite reinforcement material for instance lower in mechanical and thermal properties and highly hydrophilic which makes it deteriorate by moisture and water presence (Liu et al. 2016). With an advancement in nanotechnology, the nano-size cellulose fibres; nanocrystalline cellulose fibre (NCC) and nanofibrillated cellulose fibre (NFC), has extensively studied and found to possess various promising properties, especially after incorporates in the resin matrix for composite products. The NCC was obtained by isolation of crystalline region in cellulose chain by acid hydrolysis process. Due to highly crystalline region in NCC, it possesses unique nanoscale properties, especially on high surface area, high aspect ratio and high mechanical strength and modulus (Santamaria-Echart et al., 2016). Besides, it is also low in density and biodegradable (Siro and Plackett, 2010). With such properties, it performs better properties as a reinforcing agent in composite, or so called bionanocomposites, than composites using macro/micro size cellulose fibres (Kargazadeh et al. 2017).

Recent study conducted by Santamaria-Echart et al. (2016) shows that by incorporating 3.0 wt. % NCC fibres in waterborne polyurethane, the thermo-mechanical stability and mechanical properties of the composite film had been improved. Same trends were also observed by Robles et al. (2015) and Khoo et al. (2015) in which by incorporating 0.5 to 5.0 wt. % of NCCs in polylactic acid (PLA). Other studies that incorporating NCC in different matrices also show the remarkable properties improvement, for instance matrix from poly (vinyl acetate) (Xu et al., 2016), poly (vinyl alcohol)/polyacrylamide (Mandal and Chakrabarty, 2015), whey protein (Qazanfarzadeh and Kadivar, 2016) and natural rubber latex (Thomas et al., 2015).

The versatility of process and tailor-made functionalities of nanocellulose in bionanocomposite allows it to be applied in various products such as pharmaceutical, automotive, electronics etc. Generally, there are four approaches to incorporate nanocellulose in bionanocomposite: 1) melt compounding, 2) solvent/solution casting, 3) layer-by-layer lamination and 4) electrospinning (Kargazadeh et al. 2017; Saba and Jawaid, 2016). In early stage of bionanocomposite research, melt compounding process using thermoplastic matrices, such as polypropylene, polyethelene and polystyrene, was a preferable method to incorporate nanocellulose fibre, due to the industrial up-scalable technology and low cost (Fortunati et al., 2017). However, because of the limitations caused by particle dispersion/agglomeration, high temperature processing and polymer-fibre polarity compatibility on the melt compounding process, other type of processing technique, like solvent/solution casting leads to more option on matrix types, such as polyurethane, starts to be considered. The interface bonding/networking between nanofibres and matrix gave major effects to bionanocomposite performance (Fortunati et al., 2016). Bionanocomposite produced by solvent/solution casting was found to perform better due to enough self-organize of fibre and matrix, allowing better interface bonding/networking to occur, thus, improved the composite properties (Kargazadeh et al. 2017).

1.1.2 Jatropha oil as bio based polymer material

Besides cellulose-based materials, plant-oil also plays a key role in contributing income to Malaysia economy, especially from oil palm industries as mentioned earlier. As in November 2017, Malaysia had produced about 19.9 million tonnes of crude palm oil and palm kernel oil (MPOB, 2017). However, there are issues arise as using edible oil such as palm oil to serve non-food products. The use of edible oils as feedstocks is not a preferable option as it will create a conflict of interest (food security) in the demand and supply for food sector. It will affect the price, insufficient supply and the growth of commercial plant capacities (Bankovi´c-Ili´c et al., 2012). Realising this, since 2007 Malaysia had embarked on production of non-edible plant oil from *Jatropha curcas* purposely to serve non-food products production (Sulaiman et al. 2013). This is a very important move to ensure Malaysia maintaining its position among the world leading countries that produce plant-oil feedstock. Since then, jatropha trees were commercially planted which cover about 800,000 acres and involve around 500 nurseries and collection centres (Taib et al, 2017). In fact, Malaysia has collaborated with many other countries such as Ethiopia, Libya, Burkina Faso, Sudan, Nigeria, Ghana, Indonesia, Uganda, Chad, Turkey and Qatar for jatropha trees cultivation and development of jatropha oil-based products, such as biofuel, jet-fuel, fuel additives and nano-emulsion (Bionas, 2017). To ensure competitiveness and viability of jatropha industries, products diversification and further biotechnology improvement need to be carried out (Sulaiman et al., 2017).

Adhesive and resins matrix such as polyurethane are one of the possible products that can be produced from plant-based oil, such as jatropha oil. It is using a similar method to those derived from petro-chemicals polymers. Polyurethane has attracted a great interest due to its versatility in applications and the possibility to be synthesized with wide variety of polyols and isocyanates. Depending on the reactant, polyurethane can be fabricated to a wide range of polymers, from high performance elastomers to tough and rigid plastics (Saalah, 2015). Construction, electrical appliances and automotive industries are among the major industries that use polyurethane (Seydibeyoğlu et al., 2013). Plant oil is composed by triglyceride and contains many active sites such as double bonds, allylic carbons, and ester groups which can be introduced with polymerizable groups. Thus, making it suitable and flexible to use various processing technique, such as melt-compounding and solvent casting. Recently, many studies investigate on the use of jatropha oil for production of polyol and polyurethane, for instance, as a non-aqueous solid polymer electrolyte (Mustapa et al., 2016), waterborne polyurethane film (Saalah et al., 2015), wood adhesives (Aung et al, 2014), polyol synthesis (Hazmi et al. 2013), urethane alkyl-based polymer (Saravari and Praditvatanakit, 2013), microwave assisted coating (Alam and Alandis, 2011; 2012) and UV curing coating (Aung et al. 2014; Taib, 2017). Unlike palm oil, which has low unsaturation chemical composition, jatropha oil contains almost 80 % of unsaturated fatty acids and is possible to be functionalised to hydroxyl in polyol preparation (Saalah, 2015).

1.2 Statement of problem and hypothesis

It is to noted that, one of the major drawbacks of using neat bio-based polymer matrix is its poor mechanical properties (Seydibeyoğlu et al., 2013). Since ancient, cellulose fibres always become preferable reinforced material to enhance few properties of composite products especially on mechanical performance. Cellulose is a linear chain of repeating β-D-glucopyranose unit that connected with glycosidic bonds. It is rich in hydroxyl groups, which can create much hydrogen bonding with polymer matrix. As the nanocrystalline cellulose fibres offers large surface area and exposes more hydroxyls group, it will promote much hydrogen bonding with matrix to occur. Polyurethane is one of the preferable polymer matrix to be blended with materials that contain much hydroxyl group as it will react with N=C=O groups of diisocyanates, forming the strong interfacial bonds (Oprea et al., 2016). Numbers of studies have demonstrated on using biopolyurethane synthesized from different plant oils and reinforced with cellulose fibres show the properties improvement. Oprea et al. (2016) had conducted a study of cellulose composite using polyurethane that synthesized from castor oil. It shows that hydroxyl groups had remarkably increased the interfacial bonding in the composite, thus, enhanced the composite properties, especially on the thermal stability and Young modulus. In fact, it also shows a fungal deterioration for composite with high content of cellulose, making it a potential eco-friendly biomaterial. Glowinska and Datta (2016) and Seydibeyoğlu et al., (2013) had synthesized soy bean oil polyurethane as matrix for cellulose composite films. Their FTIR analysis showed that cellulose content had affected the chemical properties of biopolyurethane composite. The mechanical, thermo-mechanical properties and microscopic images confirmed that a good interfacial bonding of matrix and cellulose fibres were formed in the composites.

There are a number of studies on polyol and polyurethane from jatropha oil have been carried out for various applications. However, none of the studies investigates on the production of composite film by incorporating cellulose fibre as a reinforcement material in jatropha oil-based polyurethane matrix. Therefore, the study to incorporate cellulose fibre in jatropha oil-based polyurethane is essential. As shown by previous works that the reinforced cellulose fibres in polyurethane from other types of plant oil, it is expected by reinforced the jatropha oil-based polyurethane with cellulose fibres will give the similar effects on the properties of composite films. The effects of cellulosic fibre at different contents and sizes in jatropha oil polyurethane will be investigated. In this work, a green bionanocomposite polyurethane film using biopolymer materials were produced.

1.3 Aims and objectives of study

This study aims to develop a fully biopolymer composite film by reinforcing the jatropha oil-based polyurethane using micro and nanocrystalline cellulose fibres. The optimum contents of micro and nanocrystalline cellulose fibres were investigated by incorporating both of fibres at different loading contents in Jatropha oil-based polyurethane matrix. Therefore, the aim of this study is met by considering the following specific objectives:

1. To examine properties of microcrystalline celluloses (MCC) and isolated nanocrystalline celluloses (NCC);

2. To investigate the influence of MCC and NCC fibres at different loading contents on the physical and morphological properties of Jatropha oil-based polyurethane (JOPU) composite film.

3. To determine the effects of different loading contents of MCC and NCC fibres on the chemical, thermal and mechanical properties of JOPU composite films

4. To evaluate the water wettability and uptake properties of JOPU composite films with different MCC and NCC loading contents.

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