UNIVERSITI PUTRA MALAYSIA

BIODEGRADABLE COMPOSITE FILMS FROM MODIFIED SUGAR PALM (Arenga pinnata (Wurmb) Merr.) STARCH FOR FOOD PACKAGING APPLICATIONS

MUHAMMED LAMIN SANYANG

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By

MUHAMMED LAMIN SANYANG

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

December 2015

DEDICATION

This thesis is exclusively dedicated to:

My beloved mother for her invaluable sacrifices, encouragements and support throughout my life
&
My awesome wife for her love, patience and understanding

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfil4ment of the requirement for the degree of Doctor of Philosophy

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Chairman : Mohd Sapuan Salit, PhD, PEng
Institute : Advance Technology

Rapid exhaustion of petroleum resources coupled with increasing awareness of global environmental problems related to the use of conventional plastics; are the main driving forces for the widespread acceptance of biopolymers as green materials. Biopolymers have attracted considerable attention due to their environmentally friendly and sustainable nature. Sugar palm is a multipurpose tree grown in tropical countries and it is regarded as a potential source for natural fibers and biopolymer. Sugar palm starch extracted from sugar palm tree can be utilized for preparing biodegradable starch based films. However, the inherent drawbacks associated with starch based films such as brittleness, poor water vapor barrier and high moisture sensitivity which in turn limit their wide application in the packaging industry. In order to address such drawbacks, three modification techniques were employed in this study: (1) plasticized with different plasticizers and concentration, (2) incorporated with another polymer or (3) reinforced with cellulose fibers to enhance functional properties of the resulting sugar palm based films. Consequently, sugar palm starch (SPS) films were successfully developed using solution casting method. The effect of different plasticizer types (glycerol (G), sorbitol (S) or glycerol-sorbitol combination (GS)) with varying concentrations (0 – 45 %) on the physical, mechanical, thermal and water barrier properties of SPS based films were evaluated. Regardless of plasticizer types, the tensile strength of plasticized SPS films decreased, whereas their elongation at break (E%) increased as the plasticizer concentrations were raised. However, the E% for G and GS-plasticized films significantly decreased at higher plasticizer concentration (45% w/w) due to anti-plasticization effect of plasticizers. Change in plasticizer concentration showed insignificant effect on the thermal properties of S-plasticized films. The glass transition temperature of SPS films slightly decreased as the plasticizer concentration increased from 0 – 45 %. The plasticized films exhibited increased water vapor permeability values, irrespective of plasticizer types. Furthermore, the influences of glycerol-sorbitol plasticizer combination on the stability of functional properties of SPS based films with respect to storage time were investigated. Functional properties such as mechanical, thermal and water barrier properties were studied, in addition to crystallinity and moisture content of plasticized films after different storage time (1, 3 and 6 months) at constant temperature and relative humidity. The

obtained results demonstrated significant changes on the functional properties of SPS films plasticized with only glycerol or sorbitol during storage. However, the combination of glycerol and sorbitol plasticizers helps to improve the stability, acceptability and shelf-life of SPS films. In addition, the development and characterization of environmentally friendly bilayer films from sugar palm starch (SPS) and poly (lactic acid) (PLA) were also investigated. The SPS-PLA bilayer films and their individual components were characterized for their physical, mechanical, thermal and water barrier properties. The incorporation of PLA layer significantly improved the mechanical, water vapor permeability as well as reduced the water uptake and solubility of bilayer films which was attributed to the hydrophobic characteristic of the PLA layer. Lastly, the effect of sugar palm derived cellulose loading on the physical, mechanical and water barrier properties of sugar palm cellulose fiber reinforced SPS composite films were evaluated. The addition of sugar palm cellulose from 1 to 10 % significantly improves the mechanical and water vapor permeability properties of the reinforced SPS composite films compared to virgin SPS films. Overall, the results obtained from the current research manifested that modified sugar palm starch with glycerol-sorbitol plasticizer, poly (lactic acid) in the case of SPS-PLA bilayer films, and the addition of sugar palm cellulose significantly increase the functional properties and enhances the suitability of SPS based films for food packaging. In conclusion, modified sugar palm starch based films are potential biodegradable materials for food packaging applications.

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

FILEM KOMPOSIT BOLEH BIOROSOT DARIPADA KANJI ENAU (*Arenga pinnata (*Wurmb) Merr.) UNTUK APLIKASI PEMBUNGKUSAN MAKANAN

Oleh

MUHAMMED LAMIN SANYANG

Disember 2015

Pengerusi : Mohd Sapuan Salit, PhD, PEng
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Kekurangan sumber petroleum yang semakin pesat serta peningkatan kesedaran mengenai masalah alam sekitar global yang berkaitan dengan penggunaan plastik konvensional; adalah daya penggerak utama bagi penerimaan secara meluas terhadap biopolimer sebagai bahan hijau. Biopolimer telah menarik perhatian kerana sifatnya yang mesra alam dan mampan. Enau adalah pokok pelbagai guna yang tumbuh di negara-negara tropika dan dianggap sebagai sumber yang berpotensi untuk gentian semula jadi dan biopolimer. Kanji enau yang diekstrak dari batang pokok enau boleh digunakan untuk menyediakan filem *boleh* biorosot yang berasaskan kanji. Walau bagaimanapun, kelemahan yang wujud berkaitan dengan filem berasaskan kanji seperti kerapuhan, halangan wap air yang lemah, dan sensitiviti terhadap kelembapan yang tinggi menghadkan aplikasinya dalam industri pembungkusan. Dalam usaha untuk menangani kelemahan tersebut, tiga teknik pengubahsuaian telah digunakan dalam kajian ini: (1) memplastikkan dengan bahan pemplastik yang berbeza jenis dan kepekatan, (2) menggabungkan dengan polimer lain atau (3) diperkukuh dengan gentian selulosa untuk menambahbaik ciri-ciri fungsi filem berasaskan kanji enau. Oleh yang demikian, filem kanji enau telah berjaya dibangunkan dengan menggunakan kaedah penuangan larutan. Kesan jenis pemplastik yang berbeza (gliserol (G), sorbitol (S) atau gabungan gliserol-sorbitol (GS)) dengan kepekatan yang berbeza-beza (0 - 45%) ke atas sifat fizikal, mekanikal, haba dan halangan air filem berdasarkan SPS telah dinilai. Tanpa mengira jenis pemplastik, kekuatan tegangan filem SPS menurun, manakala pemanjangan ketika putus (E%) meningkat apabila kepekatan pemplastik ditingkatkan. Walau bagaimanapun, E% untuk filem yang diplastikkan oleh G dan GS menurun dengan ketara pada kepekatan pemplastik yang lebih tinggi (45% w / w) disebabkan oleh kesan anti-pemplastikkan oleh bahan pemplastik. Perubahan dalam kepekatan pemplastik menunjukkan kesan yang tidak ketara pada sifat haba filem yang diplastikkan oleh S. Suhu peralihan kaca filem SPS sedikit menurun apabila kepekatan pemplatik meningkat 0-45%. Filem-filem yang diplastikkan mempamerkan peningkatan nilai kebolehtelapan wap air, tanpa mengira jenis pemplastik. Tambahan pula, pengaruh gabungan pemplastik gliserol-sorbitol terhadap kestabilan sifat berangkap filem berasaskan SPS telah disiasat berdasarkan masa penyimpanan. Sifat berangkap seperti mekanikal, haba dan ciri-ciri halangan air telah dikaji, sebagai tambahan kepada penghabluran dan kelembapan kandungan

filem selepas masa penyimpanan yang berbeza (1, 3 dan 6 bulan) pada suhu malar dan kelembapan relatif. Keputusan yang diperolehi menunjukkan perubahan yang besar ke atas sifat-sifat berangkap filem SPS semasa penyimpanan. dengan hanya gliserol atau sorbitol sebagai pemplastik Walau bagaimanapun, gabungan gliserol dan sorbitol membantu meningkatkan kestabilan, penerimaan dan jangkahayat untuk simpanan filem SPS. Di samping itu, pembangunan dan pencirian filem dwilapisan mesra alam daripada kanji enau (SPS) dan poli (asid laktik) (PLA) turut dikaji. Filem dwilapisan SPS-PLA dan komponen individu mereka telah dikaji untuk sifat fizikal, mekanikal, haba, dan halangan air. Penggabungan lapisan PLA telah meningkatkan sifat mekanikal, kebolehtelapan wap air, serta mengurangkan penyerapan air dan keterlarutan filem dwilapisan yang disebabkan oleh sifat hidrofobik lapisan PLA. Akhir sekali, kesan penambahan selulosa daripada enau pada sifat fizikal, mekanik dan halangan air filem komposit SPS bertetulang selulosa telah dinilai. Penambahan selulosa enau dari 1 hingga 10% telah meningkatkan sifat mekanikal dan kebolehtelapan wap air daripada filem komposit SPS bertetulang berbanding filem SPS tulen. Secara keseluruhan, keputusan yang diperolehi daripada penyelidikan semasa menunjukkan bahawa kanji enau yang diubahsuai dengan pemplastik gliserol-sorbitol, poli (asid laktik) untuk filem dwilapisan SPS-PLA, dan penambahan daripada selulosa enau menunjukkan peningkatan ketara bagi sifat berangkap dan meningkatkan kesesuaian filem berasaskan SPS untuk pembungkusan makanan. Kesimpulannya, filem berasaskan kanji enau yang diubah suai adalah bahan mesra alam yang berpotensi untuk kegunaan pembungkusan makanan.

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JazakAllahu Khairan!

I certify that a Thesis Examination Committee has met on 31 December 2015 to conduct the final examination of Muhammed Lamin Sanyang on his thesis entitled "Biodegradable Composite Films from Modified Sugar Palm (*Arenga pinnata* (Wurmb) Merr.) Starch for Food Packaging Applications" 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 Doctor of Philosophy.

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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 Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Signature: _____
Name of Member of Supervisory Committee: Dr Sahari Japar

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LIST OF ABBREVIATIONS

ATR	Attenuated total reflectance
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTGA	Derived Thermal-gravimetric analysis
E	Elongation at break
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
G	Glycerol
GS	Glycerol-sorbitol
HIPS	High impact polystyrene
HSE	Health safety and Environment
IFSS	Interfacial shear strength
NaOH	Sodium hydroxide
S	Sorbitol
SEM	Scanning electron microscope
SPC	Sugar palm cellulose
SPF	Sugar palm fiber
SPS	Sugar palm starch
TGA	Thermal-gravimetric analysis
TM	Tensile modulus
TPS	Thermoplastic starch
TS	Tensile strength
UP	Unsaturated polyester
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1. Background

1.1.1. Biobased packaging plastics

Recently, keywords such as “biobased”, “biodegradable”, “biocompatible”, “compostable”, “renewable”, “sustainable”, “green”, “environmentally friendly”, “eco-friendly”, and “biopolymers” are common sight in the packaging-related literature. This explicitly manifested the growing awareness and concern of people regarding environmental issues triggered by non-biodegradable and non-renewable plastics as well as the rapid depleting fossil fuel reserves (Suppakul et al., 2013; Tang et al., 2012; Rhim and Ng, 2007).

The plastic industry has been confronted with continuous pressure from the government, consumers and media; compelling the industry to develop more sustainable products (Mohan, 2014). The plastic industry and more specifically the plastic packaging industry also responded to these new stringent environmental protection laws and has commence innovating sustainable packaging (bioplastics) products. According to the report of Mohan (2014), the bioplastic market was anticipated to reach a value of US$3.94 billion in 2014. The drastic growth in the commercialization of biobased packaging materials is primarily accelerated by factors such as (1) greater environmental awareness, (2) the depletion of petrochemical resources, (3) government laws and company policies, and (4) suitable technology.

Environmental awareness

The growing environmental awareness throughout the world has attracted the development of environmentally friendly plastic materials which are biodegradable and from renewable sources. Despite the numerous merits attached with the use of petroleum based plastics, they bring about severe environmental effects. High resistance to biodegradation is the root cause of their undesirable environmental impacts. The high recalcitrant nature of petroleum based plastics to biodegradation has posed great challenge for municipal solid waste management companies and contributed to the rapid exhaustion of landfills. Therefore, several researches have been conducted to develop environmentally friendly plastics from renewable sources. Over the years, there is mounting interest in the development and use of biobased packaging materials. Of late, starch-based packaging materials have emerged in the biobased plastic market and are becoming more commercialized. Their usage is expected to surpass 30,000 tons (annually) within the subsequent years ahead (Weber et al., 2002). The consumption of such environmentally friendly packaging materials is on the growth, especially in countries where landfill is the primary waste management option (Cha and Chinnan, 2004). Municipal solid waste generation increased 37 % from 1988 to 2005, and packaging materials contributed 31.2 % of the total solid waste (Tang et al., 2012). Furthermore, food packaging alone covers

almost two-thirds of the total packaging waste by volume (Weber et al., 2002; Cha and Chinnan, 2004). Thus, exploring biopolymer based materials for food packaging is a potential mitigation tool to address environmental pollution from non-biodegradable food packaging materials.

Depletion of petroleum resources

Besides minimizing the accumulation of plastics in the environment, the use of biodegradable packaging materials also help to shrink reliance on fossil fuel for better sustainability (Rhim et al., 2013). With an annual grow of approximately 5 %, the current global consumption of plastics is above 200 million tonnes (AnkKobar and Us, 2013). Still now the packaging industry heavily depends on crude oil for the production of plastics. This clearly manifested how dependent the packaging and plastic industry are on crude oil. Consequently, the increasing price of crude oil has significant influence on the plastic market. Hence, to overcome the dependence on petroleum-based polymers, attempts have been made to utilize 100% renewable and biodegradable biopolymers in the production of biopackaging materials. Biodegradable plastics from renewable resources help to preserve the non-renewable fossil fuel resources and further enhance sustainable development. The biobased plastic market is gradually exiting its infancy and taking over the petroleum-based plastic market at a growth rate of 30% annually (Arvanitoyannis et al., 1999; Fang and Fowler, 2003).

Government laws and company policies

Single-use consumer packaging materials produced from non-biodegradable plastics represents huge volume of the size of a typical landfills. It is believed that the amount of packaging waste generated in industrialized countries in a single day is sufficient to fill up a space equivalent to the Sears Tower (Chicago, USA), which was once the tallest building in the world (Imam et al., 2008).In view of the numerous environmental problems posed by petroleum-based plastics, governments of many developed countries enacted environmental policies that will help mitigate the current scenario. Most of these laws are constituted to device means of minimizing the use of non-biodegradable plastics which continued to accumulate in landfills or disposed in water bodies, which eventually poses serious impact on marine life. This provides an excellent opportunity for biobased plastics to be adopted for the replacement of petroleum-based plastics in the packaging industry.

Due to the unsustainable waste disposal in landfills, governments of several nations established laws to promote the use of recyclable and/or biobased green products. Take the case of the ‘producer pays’ principle, it was designed to encourage manufacturers to take responsibility for their products throughout their whole life cycle (Fowler et al., 2006). Such laws will not only stimulate enhancement of product recyclability, but will also offer better opportunities for the utilization of biobased materials as raw material for the manufacturing of these products. In the case of Selangor state (Malaysia), the initiation of ‘Selangor no plastic bag day’ every Saturday’, which was launched in 2010 (Figure1.1)has motivated the public to resort to recyclable bags and also promotes the use of environmentally friendly plastics made from biobased resources. The campaign has assisted in saving about 5 million plastic bags within 2 years (2010 – 2012). Thus, the state government was

planning to extend the campaign to three days, weekly (Koon, 2012). More and more countries and states follow in the banning of grocery plastic bags, which are responsible for the so called 'white pollution' across the globe (Nampoothiri et al., 2010). These activities provided biobased plastics the opportunity to gradually substitute conventional plastics.

Figure 1.1: Logo for 'Selangor no plastic bag day' every Saturday'

Several companies and institutions also have designed sustainability regulations in their Health Safety and Environment (HSE) policies, which highlight the firm's environmental responsibilities to both its employees and to the society they operating. Most of these firms are of the perception that the adoption of these policies, which may possibly include the use of biobased materials, will elevate their reputation in the eyes of the consumers, who have demonstrated their growing awareness and concern for environmental issues. For example, Universiti Putra Malaysia (UPM) is advocating for a 'Green Campus' and among the established policies is 'just to say no to plastic bag' as shown in Figure1.2. As such, the UPM clinic (particularly the pharmacy unit) abstains from providing plastic bag to patients. These stringent policies promote the production and usage of biobased plastics.

In summary, the main driving factor for the commercialization of biodegradable plastics in many countries is government laws related to environmentally benign products, in the form of a ban or restrictions and the recommendation of certain type of products. Most of the time, these laws are meant to address specific environmental concerns (Ren, 2003).

Figure 1.2: UPM advocates for a 'Green Campus'

Suitable technology

Increase commercialization of biobased plastics can help to reduce tremendous environmental threats posed by petroleum-based plastics. Many plastic and packaging industries ventured into biobased plastics using conventional plastic processing technologies. The only consideration is that the processing parameters of the equipment need to be adjusted to suit the characteristics of each bioplastic type. This helps the company to save vast amount of money.

The techniques for manufacturing biopolymers are all established polymer-manufacturing methods. However, the control and application of these techniques must be different to march with certain factors associated with exploiting the advantages of biopolymers .Though, the manufacturing procedures shows specific fundamental similarities, the major varying factor depends on whether a thermoset or thermoplastic biopolymer is to be processed (Jamshidian et al., 2010).

Injection moulding is one of the most commonly used technologies for packaging plastic manufacturing. The processing conditions for biopolymers using injection moulding have less damage to polymer. On the contrast, the most difficult in continues processes such as extrusion, is the process in which the extrudate is stretched like in the case of film blowing. The limiting factors for the processing of biopolymers and petroleum based polymers are all the same (i.e. degradation at higher temperature and shear). However, these limits are somehow narrower at the upper limits for biopolymers. When these upper limits are exceeded, it results to the degradation of biopolymers; which leads to mould defects such as discoloration, weld lines, or strong odor in the final product (Johnson et al., 2003; Jamshidian et al., 2010).

1.2. Problem statement

The swift growth of new green materials as eco-friendly packaging films is accelerated by factors such as greater environmental awareness, societal concerns, governmental policies and the depletion of petrochemical resources. The disposal of petroleum based plastics after their intended life span has become a huge global environmental issue which requires immediate attention. The two most implemented disposal alternatives are land filling and incineration. However, landfill spaces are drastically decreasing due to the heavy ongoing waste disposal. The increasing environmental pollution due to the use of abundant plastics and emissions during incineration greatly contributes to environmental health problems. Consequently, government policies regarding the use of non-renewable and non-biodegradable materials are becoming more stringent over the years, to maintain healthy environment for the future generation.

Most of the polymers used in packaging are still derived from petroleum. The extensive usage of petroleum based materials promotes CO_2 emission; which in turn contributes to global climate change. Furthermore, the production of fossil-based materials like petroleum from biomass takes millions of years. Thus, petroleum based materials are considered to be non-renewable and non-sustainable. Hence, to overcome the dependence on petroleum-based polymers, attempts have been made in this work to utilize 100% renewable and biodegradable biopolymer from sugar palm tree.

Sugar palm is a multipurpose tree found in most South East Asian countries and it is regarded as a potential source of natural fiber and biopolymer. However, such a bio-source is still underutilized and, thus, very limited studies have been reported related to their development as a green packaging material. Hence, sugar palm starch (SPS) was modified and employed in the current study to develop fully biodegradable films and composite films as environmentally friendly packaging material for the food industry.

Of late, Sahari et al. (2014) conducted a significant study related to the extraction and characterization of SPS biopolymer derived from sugar palm tree. The relevant properties of SPS such as chemical properties, thermal properties, particle size and morphological surface were investigated to explore their potential as a new alternative biopolymer. The starches isolated from sugar palm tree contained comparable amounts of amylose (37.60%) which was higher than tapioca, sago, potato, wheat and maize. The results showed significant differences in the chemical content as well as in the granule sizes of SPS. Thermal characteristic studies using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that SPS was thermally stable than other starches. The study highlighted SPS as a suitable biopolymer in preparing bioplastics for various applications including food packaging.

Sugar palm starch like most other biopolymers is hydrophilic in nature due to either their hydroxyl or polar groups. The major challenges for the development of starches as packaging films are the shortcomings related to brittleness, processability, high moisture sensitivity, quick retrogradation, poor mechanical and barrier properties (Figure 1.3). In order to transform native sugar palm starch into high performance

thermoplastic starch for packaging application, the aforementioned drawbacks should be addressed. Some of the approaches employed to tackle these roadblocks are; (1) the addition of different types and concentrations of plasticizer(s) into the starch matrix, (2) the combination of sugar palm starch with other polymers that possess better functional properties, and (3) the incorporation of cellulose fibers. The implementation of such modifications on the sugar palm starch may contribute to the improvement of its functional properties as well as help in optimizing its full potential as an effective food packaging material.

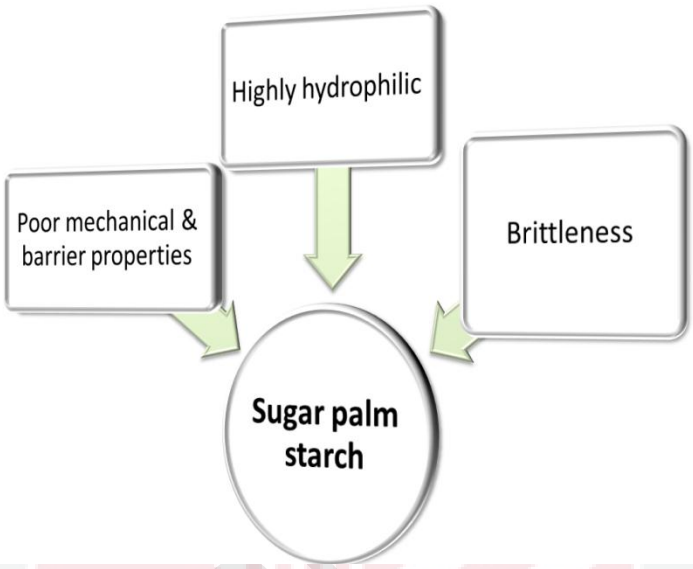

Figure 1.3: Main drawbacks of sugar palm starch films

1.3. Research objectives

The overarching aim of this current study is to develop and characterize environmentally friendly composite films based on modified sugar palm (*Arenga pinnata*) starch. The specific objectives are:

1. To evaluate the effect of plasticizer type and concentration on the properties of SPS based films.
2. To study the effect of storage time on the properties of plasticized SPS films.
3. To develop an expert system for selecting the most suitable biobased polymer material for food packaging. The selected material is to be utilized with SPS to develop bilayer films of different ratio.
4. To develop and characterize bilayer films from sugar palm starch and the selected biobased polymer in specific objective 3, at different combination ratios.
5. To investigate the effect of sugar palm cellulose fiber loading on the properties of plasticized SPS film composites.

1.4. Significance of study

a. The findings from the current study are expected to enhance the knowledge in developing high performance biodegradable films derived from sugar palm starch for food packaging.
b. It is also expected that the development of such environmentally friendly packaging films from sugar palm starch may help to address environmental problems which emanate from the disposal of non-biodegradable plastics. Hence, they could serve as good alternative to petroleum based packaging films.
c. Problems associated with the use of synthetic polymers and polymer composites can be alleviated by the use of 100% biodegradable polymer films or composite films, where the matrix (SPS) and the fiber (sugar palm cellulose fiber) are both from a single source (sugar palm tree).
d. In term of waste management issue, this research provides platform for utilizing wastes from agricultural products into fibers and biopolymers.
e. The successful development of such green materials from sugar palm tree would provide opportunities to improve the standard of living of the sugar palm tree farmers in Malaysia by generating non-food source of economic development for rural areas.
f. This study may also add to the effort to unveil the potential of using sugar palm starch and fiber in developing green products; else, such abundant bioresources may be underutilized (Figure1.4).

Figure 1.4: **Significance of research on sugar palm tree**

1.5. Scope of study

In this work, sugar palm starch and fiber were manually extracted from the sugar palm tree. The obtained SPS was plasticized during the film preparation process using different plasticizer type (glycerol, sorbitol and glycerol – sorbitol combination) and concentration (0 – 45 %) to overcome the brittleness and enhance the properties of SPS films. Characterization of their physical, mechanical, thermal and water barrier properties were performed. The film samples were later stored for different storage durations (1, 3 and 6 months) at constant relative humidity (50%) and temperature (25 °C) to investigate the effect of storage time on the physical, mechanical, thermal and water barrier properties of different plasticized SPS films. The best plasticized SPS film with outstanding functional properties as well as can maintain good properties during long-term storage was spotted out for further modification.

At this stage, an expert system was developed using Exsys Corvid software to select a suitable biobased polymer with superior functional properties to help in arresting the drawbacks associated with SPS films. The selected polymer (PLA) was incorporated with the best plasticized SPS film in the form of bilayer films, instead of blending the two polymers. No agents or additives were utilized in the modification of the surfaces of individual components of the bilayer films. The physical, mechanical, thermal and water barrier properties of the bilayer films were investigated. Finally, the sugar palm cellulose microfibers were extracted from sugar palm fibers and the morphology of the obtained cellulose microfibers was characterized through field emission scanning electron microscope (FESEM), respectively. The characterized cellulose microfibers were use as reinforcement for SPS films to improve their properties. Thus, the effect of sugar palm cellulose loading on the physical, mechanical and water barrier properties of SPS based composite films was carried out.Figure1.5 shows the scope and work flow of the current research. The numbers (1 – 5) in Figure 1.5 indicates the different specific research objectives covered in this work, whereas the symbol (*) illustrates the different raw materials manually extracted from sugar palm tree.

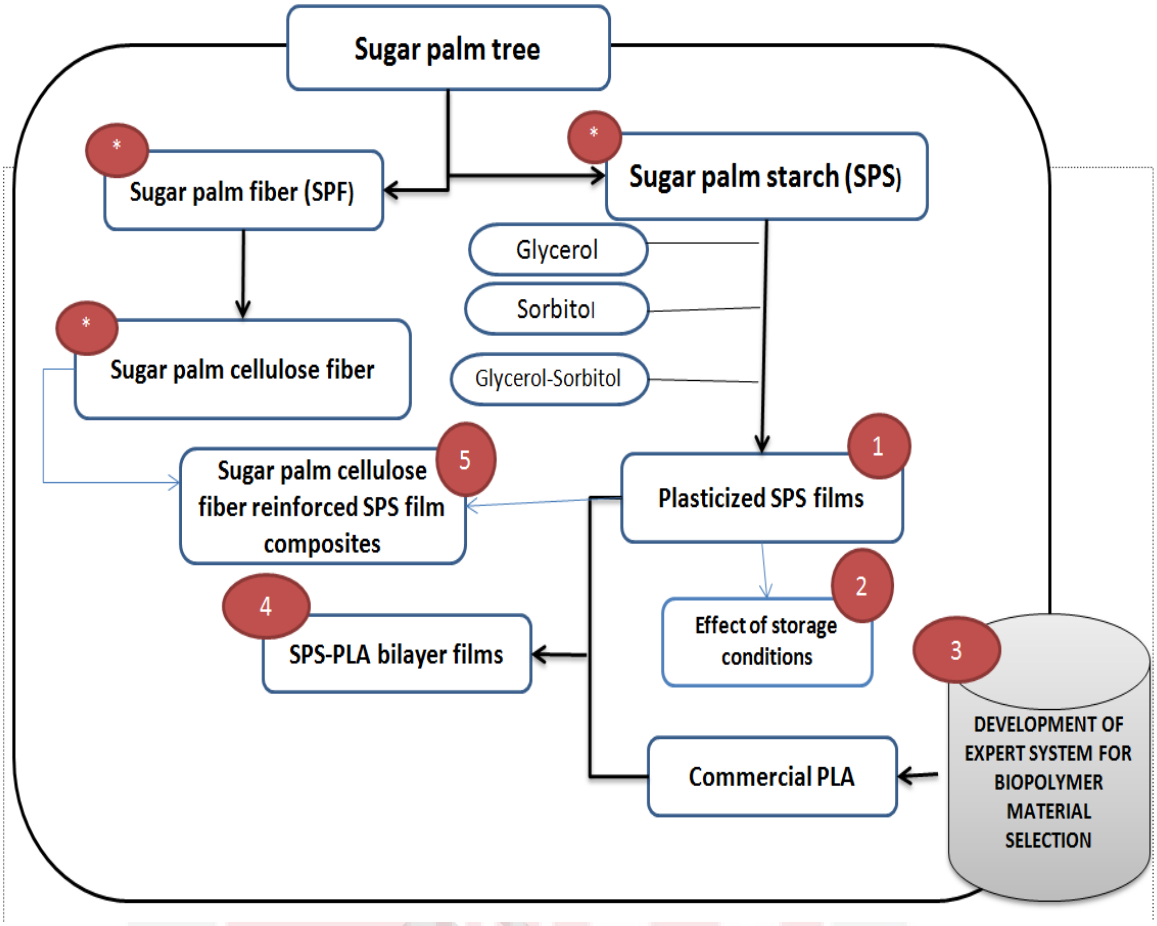

Figure 1.5:Research scope

1.6. Structure of thesis

The layout of this thesis is in accordance with Universiti Putra Malaysia alternative thesis format based on publications, in which each research chapter (3 – 9) represent a separate study that has its own: 'Introduction', 'Materials and methods', 'Results and discussion', and 'Conclusion'. Hence, it is important to note that there is no separate chapter dedicated for only the methodology. The details of the thesis structure are presented beneath.

Chapter 1
The problems that necessitate this research as well as the research objectives were clearly highlighted in this chapter. In addition, the significant contribution and scope of this study were also elucidated within the chapter.

Chapter 2
A comprehensive literature review on essential areas connected to the topic of this thesis was presented in this chapter.

Chapter 3
This chapter presents the article entitled "**Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*arenga pinnata)* starch for food packaging".** In this article, the effect of

different plasticizer type (glycerol, sorbitol, and glycerol: sorbitol) and concentrations (0, 15, 30 and 45 %) on the physical properties of sugar palm starch based films was investigated.

Chapter 4

This chapter entails the second article entitled "**Effect of plasticizer type and concentrationon tensile, thermal and barrier properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch".**The effect of different plasticizer types (glycerol (G), sorbitol (S) and glycerol-sorbitol (GS) combination) with varying concentrations (0, 15, 30 and 45, *w*/*w*%) on the tensile, thermal and barrier properties of sugar palm starch (SPS) films was evaluated in this chapter.

Chapter 5

In this chapter, the article entitled "**Effect of plasticizer type and concentration on dynamic mechanical properties of sugar palm starch based films**" is presented. The effect of different plasticizer types (glycerol (G), sorbitol (S) and glycerol-sorbitol (GS) combination) with varying concentrations (0, 15, 30 and 45, w/w %) on the dynamic mechanical properties of sugar palm starch (SPS) films were evaluated in this article.

Chapter 6

This chapter presents the article entitled "**Effects of ageing: Improved stability of sugar palm (*arenga pinnata*) starch based films during storage".** In this article, the influences of combining glycerol and sorbitol as plasticizer on the stability of functional properties of sugar palm starch (SPS) based films were investigated. Functional properties such as mechanical, thermal and barrier properties were studied, in addition to crystallinity and moisture content of plasticized films after different storage time (1, 3 and 6 months) at constant temperature and relative humidity.

Chapter 7

The focus of this chapter is on a work entitled **"Development of expert system for biobased polymer material selection: Food packaging application".** In this paper, an expert system was developed using Exsys Corvid software to select suitable biobased polymer materials for food packaging. The selected material is intended to be utilized in preparing a bilayer film with SPS (presented in chapter 8).

Chapter 8

This chapter presents the sixth article entitled "**Development and characterization of sugar palm starch and poly (lactic acid) bilayer films".** The preparation of bilayer films based on sugar palm starch and poly (lactic acid) was discussed in this paper. Furthermore, the effect of applying PLA layer at different proportion (0, 20, 30. 40, 50 and 100%) on the physical, mechanical, thermal and water barrier properties of SPS films were documented.

Chapter 9

"**Effect of sugar palm derived cellulose reinforcement on mechanical and water barrier properties of sugar palm starch biocomposite films"** is the title of the research article presented in this chapter. The preparation of biocomposite films and their characterization to investigate the effect of sugar palm cellulose fiber loading

effect (0, 1, 3, 5 and 10 %) on the properties of sugar palm starch reinforced cellulose biocomposite films were carried out.

Chapter 10
Finally, the overall conclusions from the various research articles as well as relevant suggestions for future research were presented in this chapter.

1.7. Research methodology flow

Figure 1.6 shows the research methodology flow for this thesis. The methodology flow covers every single experiment conducted in this work; ranging from the sugar palm starch and fiber extraction to film development and characterization. The photographic images of most equipment used for characterizing the physical, morphology, mechanical and thermal properties of film samples are presented in Appendix A.

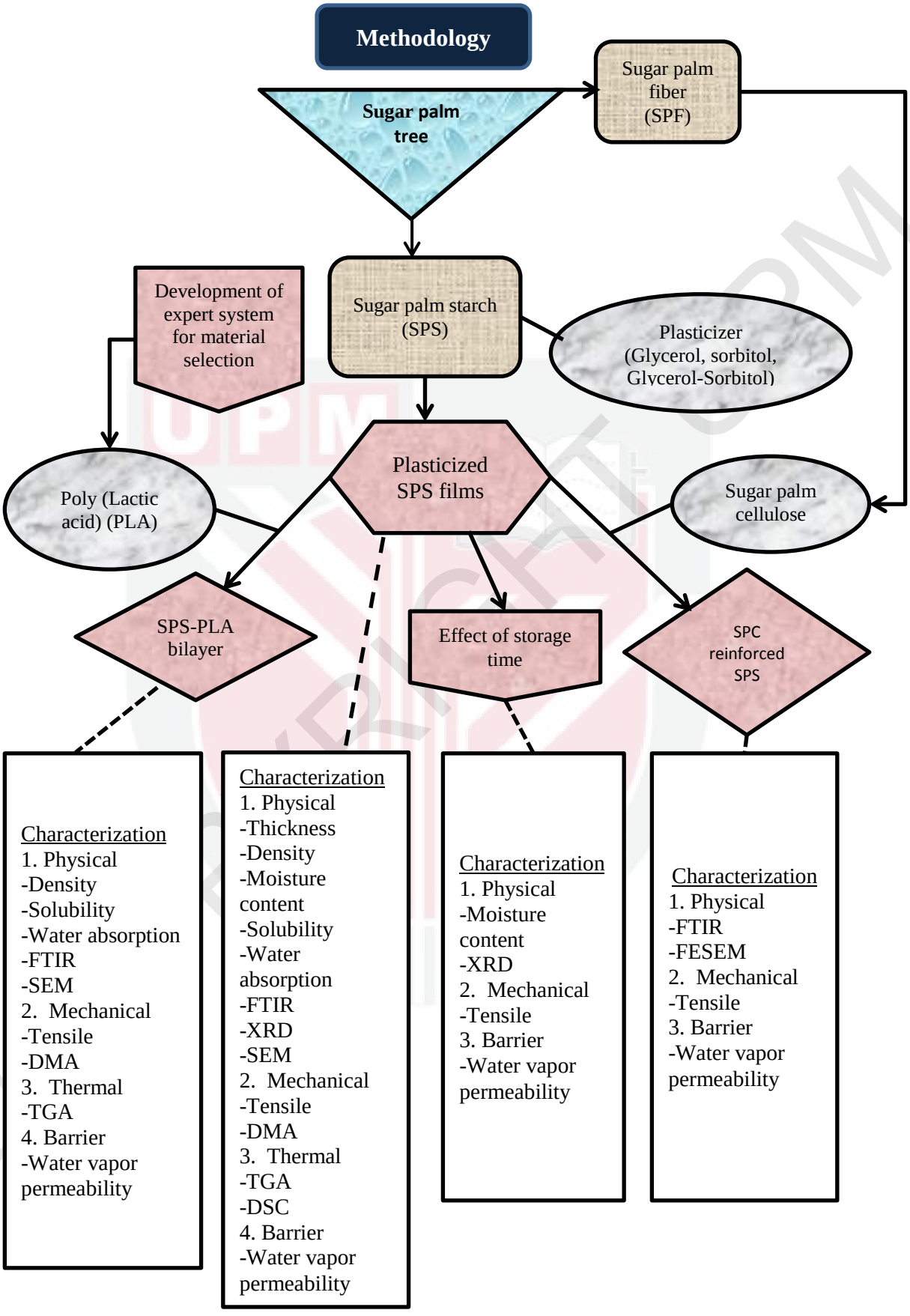

Figure 1.6: Research methodology flow

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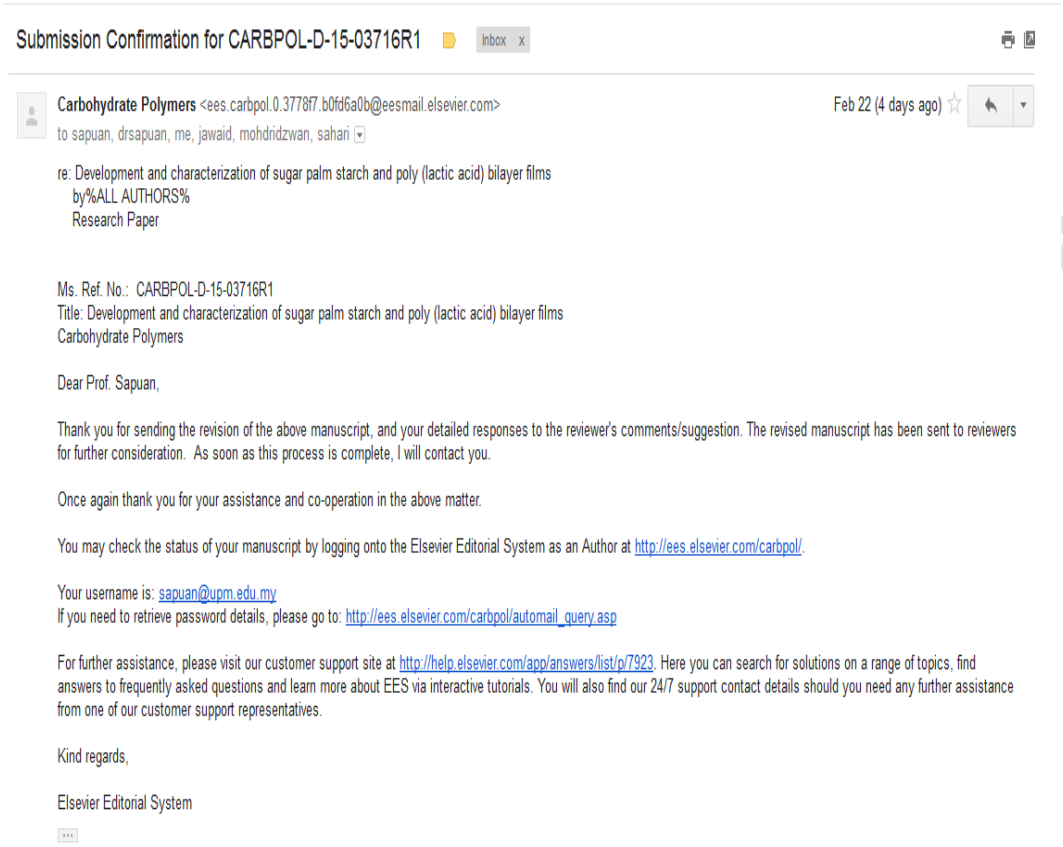

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CHAPTER 9

EFFECT OF SUGAR PALM DERIVED CELLULOSE REINFORCEMENT ON MECHANICAL AND WATER BARRIER PROPERTIES OF SUGAR PALM STARCH BIOCOMPOSITE FILMS

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Abstract

In this study, sugar palm-derived cellulose (SPC) composites were prepared and utilized as reinforcement material to improve the mechanical and water vapor barrier properties of sugar palm starch (SPS)-based films. Cellulose-reinforced SPS composite films (SPS-C) were prepared with different SPC loadings (1 to 10 wt. %) using a solution casting method. The mechanical properties of the composite films showed increased tensile strength and modulus, while the elongation at break decreased with SPC loading. Adding 1 wt. % SPC loading significantly improved the water vapor permeability (WVP) of the composite film by 63.53% compared with the neat SPS film. This was ascribed to the high compatibility between the SPC and SPS matrices, which was supported by the field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR) results.

Keywords: *Sugar palm; Starch; Cellulose; Biodegradable films; Composites*

9.1. Introduction

The growing environmental devastation ascribed to the disposal of packaging plastic waste has necessitated an urgent need to develop environmentally friendly packaging materials to rescue our ecosystem (Kaushik *et al.* 2010). In an effort to resolve the ongoing environmental crisis caused by non-biodegradable plastics, natural biopolymers have been investigated as potential alternatives to conventional plastics. Starch is one of the most widely available biopolymers for packaging applications. In addition to its wide availability, it is affordable, renewable, and biodegradable. Therefore, starch has attracted a great deal of attention as a promising green material as well as a potential alternative to non-biodegradable plastics (Savadekar and Mhaske 2012).

However, starch-based films for packaging have been reported to have poor mechanical strength and a low water barrier resistance (Teixeira *et al.* 2009; Bilbao-Sainz *et al.* 2011; Teac *et al.* 2013). Such drawbacks strongly limit their wide application, especially for food packaging purposes. Many studies have been undertaken by material scientists to improve the mechanical properties and enhance the water sensitivity of starch-based materials without compromising their biodegradability (Sanchez-Garcia *et al.* 2008; Müller *et al.* 2009; Dias *et al.* 2011). The addition of natural cellulose fibers during the preparation of starch composite films is an effective strategy for improving the functional properties of packaging films concurrently, as documented by various researchers (Teixeira *et al.* 2009; Teac *et al.* 2013; Slavutsky and Bertuzzi 2014). Thus, green micro/nanocomposite films are envisaged as the next-generation packaging materials.

Cellulose is a bio-based material abundantly found in natural plants. The cellulose commonly derived from cellulosic fibers is generated by plants through photosynthesis, using water and carbon dioxide in the presence of energy from sunlight (Ng *et al.* 2015). Cellulose is known to be the backbone material of the long fibrous cells embedded in hemicelluloses and lignin. The removal of hemicelluloses and lignin using different chemical treatment techniques gave rise to a new, eco-friendly fiber material: cellulose microfibers. They are readily available, inexpensive, renewable, and lightweight (Kaushik *et al.* 2010). Cellulose fibers utilized as reinforcement have been proven to enhance the performance of starch composite films by providing high thermal stability and good mechanical properties such as high tensile strength and high Young's modulus (Kaushik *et al.* 2010; Savadekar and Mhaske 2012). Furthermore, the addition of cellulose fibers has been reported to decrease the water vapor permeability of starch-based films (Müller *et al.* 2009; Dias *et al.* 2011), thus increasing their suitability for food packaging applications.

Numerous types of cellulosic reinforcements have been investigated and tested in biopolymers. Interestingly, it was found that the compatibility between the starch matrix and cellulose fibers is high, which is significant for obtaining enhanced mechanical and water sensitivity (Kaushik *et al.* 2010). Based on previous studies (Ishak *et al.* 2013), sugar palm is considered to be a good source of cellulose fiber because of its high cellulose content. Sugar palm is a multipurpose tree mostly grown in tropical countries. It serves as a potential source of natural fiber and starch for developing green composite materials. Several studies by the authors (Sanyang *et al.* 2016; Sanyang *et al.* 2015a,b) have reported on the physical, mechanical, thermal,

and water barrier properties of plasticized sugar palm starch films for food packaging applications. The results obtained from these previous studies suggest upgrading the mechanical and water vapor barrier properties of sugar palm starch films to further enhance their performance.
To the best of our knowledge, no study on sugar palm-derived cellulose has been found in the literature. Hence, the aim of the current study was to extract cellulose from sugar palm fibers and incorporate the sugar palm-derived cellulose into sugar palm starch as reinforcement material to improve the mechanical and water vapor barrier properties of sugar palm-based films.

9.2. Materials and methods

9.2.1. Materials

Sugar palm starch and fibers extracted from sugar palm tree at Jempol, Negeri Sembilan (Malaysia). Reagent grade acetic acid (CH_3COOH), sodium hydroxide (NaOH) and technical grade sodium chlorite ($NaClO_2$) OF 80% purity were purchased from LGC Scientific. Reagent grade of glycerol and sorbitol plasticizers were also obtained from the same supplier.

9.2.2. Sugar palm fiber extraction and preparation

Figure 9.1 shows the extraction and preparation process of the Sugar palm fibers (SPF) used in this work. SPF were extracted from in SPF which were extracted from different parts of the sugar palm tree (sugar palm frond, bunch, ijuk and trunk). The SPF is readily wrapped around the trunk of the tree from top to bottom. Slashing knife was utilized to manually remove SPF from the tree and the harvested SPF requires no secondary processing such as mechanical retting. In order to obtain uniform SPF size (2mm), Fritsch pulverisette mill was used for grinding and screening the SPF to the desired size.

Figure 9.1: Extraction and preparation of SPF

9.2.3. Cellulose extraction

With reference to Tawakkal et al. (2012) and Tee et al. (2013) cellulose fiber were extracted from sugar palm fibers (SPF) using two main processes, delignification and mercerization. The initial process was performed in accordance with ASTM D1104 to prepare holocellulose through chlorination or bleaching process, mainly designed for the removal of the lignin from the SPF. In this step, 20 g of SPF were rinsed with tap water to remove dust and foreign particles. The clean SPF was soaked into a 1000 ml beaker containing 650 ml of hot distilled water which was subsequently transferred to a water bath and the temperature was set at 70 °C. Thereafter, 4 ml of acetic acid and 8 g of sodium chlorite were added to the beaker after every hour for 5 hours, consecutively. The changing colour of the SPF from light brown to white indicates the level of delignification. The obtained celluloses are referred to as holocellulose which were filtered, washed and rinsed with distilled water.

The holocellulose was further treated to produce alpha-cellulose according to ASTM D1103. The holocellulose was soaked in 500 ml of 5 % w/v NaOH solution for 2 hours at 23 ± 2 °C. The produced alpha-cellulose are filtered and immerged in 500 ml of distilled water containing approximately 7 ml of acetic acid to neutralize the cellulose. The mixture was stirred for about 30 s before allowing it to settle for 5 min. Therefore, the cellulose was rinsed with water until the cellulose residue was free from acid, as indicated by a pH meter. Lastly, the cellulose denoted as SPC in the current study, was dried in an oven at 103 °C overnight.

9.2.4. Preparation of composite films

The composite films were developed using solution casting technique. An aqueous suspension of SPC was prepared by mixing known concentration of SPC (1 – 10 % on starch basis) with distilled water. The starch film-forming solution was prepared by adding 10g of SPS to 125ml of distilled water. Cellulose fibers were added to the SPS film-forming mixture and stirred at 1000 rpm for 20 min in a disperser. Thereafter, 30% of combined glycerol and sorbitol as a single plasticizer was added to the mixture under constant stirring (100 rpm) while the mixture was heated at 95°C for 15 min. The film-forming suspension was left to cool down before pouring 35 g of the suspension in each petri dish (13 cm diameter). The dishes containing the film-forming solution were placed in an oven at 40 °C for 24 hours. SPS films prepared without SPC serves as control (denoted as SPS films). Composite films with 1, 3, 5 or 10 % SPC concentration were designated as SPS-C1, SPS-C3, SPS-C5 or SPS-C10, respectively.

9.2.5. Field Emission scanning Electron Microscope (FESEM) image

The morphology of raw sugar palm fiber and sugar palm derived cellulose was investigated using field emission scanning electron microscope (JEOL JSM-7600F, Japan) at an acceleration voltage of 5 kV. The film samples were mounted on aluminium stubs with double-sided adhesive tapes. Thereafter, the samples were coated with gold to avoid charging.

9.2.6. FTIR

Infrared spectra of the film samples were analyzed using Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR). Firstly, a film sample was mounted on a sample holder in contact with ZnSe crystal and then placed on an attenuated total reflectance accessory. FTIR spectra were collected by recording 42 scans with a resolution of 4 cm^{-1} in a 4000 – 400 cm^{-1} wave range. The ZnSe crystal which possesses high reflective index was thoroughly cleaned after each measurement.

9.2.7. Tensile properties

The mechanical properties of the films were tested using a standard method D882-02 (ASTM, 2002). Tensile strength and elongation at break were determined by using Instron 3365 universal testing machine with a load cell of 30 kg. Films were cut in the form of strips with dimension of 10 mm × 70 mm. The strips were clamped between two tensile grips and the initial gauge length was set at 30 mm. Films were pulled using a crosshead speed of 2 mm/min. During the stretching, force (N) and deformation (mm) were recorded. Measurements were carried out on 10 different specimens. The mechanical properties were calculated as average value from the obtained results.

9.2.8. Water vapour permeability (WVP)

Prior to the WVP test, the film samples were conditioned in a desiccator with relative humidity of 50 % at 25 °C. The WVP test was conducted according to ASTM E96-95 with slight modifications. Circular film samples were mounted and sealed on the open mouth of cylindrical cups containing 20 g of silica gel. The test cups were measured before being kept in a relative humidity chamber (25 °C, relative humidity 75 %). The weight of the test cups were determined by periodic measurement till the equilibrium state was reached. Weight increments of the test cups were recorded and WVP was calculated as follows:

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Where *m* (g) is the weight increment of the test cup, *d* (mm) is the film thickness, *A* (m^2) is the area of film exposed, *t* (s) is the duration for permeation, and *P* (Pa) is the water vapor partial pressure across the films. The results were expressed in g mm s^{-1} m^{-2} Pa^{-1}.

9.2.9. Statistical analysis

The statistical analyses of the obtained experimental results were performed by analysis of variance (ANOVA) using Minitab 16 software. Mean comparisons were conducted using Turkey's test at a 0.05 level of significance.

9.3. Results and discussion

9.3.1. Morphology of SPC

FESEM micrographs of sugar palm fiber (SPF) and sugar palm derived celllulose (SPC) presented in Figure 9.2 revealed their homogeneity and micrometric dimensions. Digital image analysis (imageJ) was utilized to examine the diameter of both samples. The average diameter of SPF and SPC was around 43.71 ± 9 μm and 10.24 ± 3 μm, respectively. This clearly indicates that the diameter of SPC is almost four times smaller than that of SPF. The obtained diameter for SPC is in agreement with the average diameter of kenaf derived cellulose (13 μm) reported by Tawakkal et al. (2012). Elsewhere, Sonia et al. (2013) reported 10.04 μm as the average diameter of celluloses microfibers. In a separate investigation, Tee et al. (2013) also reported that the diameter of kenaf derived cellulose (17.38 μm) was four times smaller than the natural kenaf fiber (61.77 μm). The drastic reduction in the diameter of SPC can be attributed to the removal of hemicellulose and lignin through the delignification and mercerization of raw SPF.

It can be seen that the surface topography of the rod-like SPFs are rough with pore-like spots that appears almost in regular intervals. Similar spots were reported by Ticoalu et al. (2012) with respect to the surface of sugar palm fibers and coir. According to their report, these visible spots on the surface of the fibers are known as tyloses which cover the pits on the cell walls. Nevertheless, after removing the hemicellulose and lignin of SPF, the derived SPC shows a relatively smooth surface with parallel lines running along the length of the cellulose. Thus, the topography of the SPC can be described as a groovy surface topography. Similar reports were documented regarding the surface appearance of many natural fiber derived cellulose (Sgriccia, Hawley, & Misra, 2008; Tawakkal et al., 2012; Tee et al., 2013).

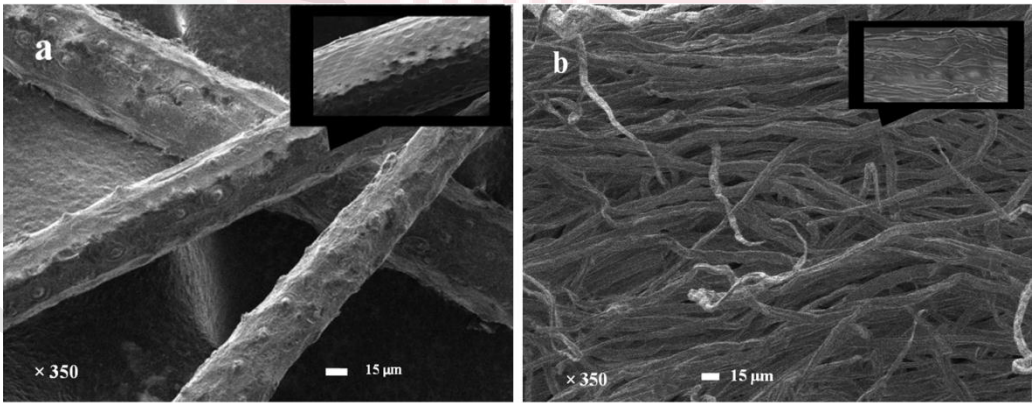


Figure 9.2: FESEM micrographs of raw sugar palm fiber (a) and sugar palm derived cellulose (b)

9.3.2. FTIR of composite films

Figure 9.3 shows the infrared (IR) spectra of neat SPS and SPS-C composite films with different SPC concentration. The broad peak of SPS film observed at 3600 – 3020 cm^{-1}corresponded to O–H group, whereas the peak at 2950 cm^{-1} was assigned to C–H stretching. The small peak displayed at 1680 cm^{-1} was attributed to the C=O stretching. The band at 1305 cm^{-1} was related to O–H of water. Similar peak was reported by Bourtoom and Chinnan (2008) with rice starch film. The sharp peak at 1004 $cm^{-1}$was associated with C–O bond of C–O–C groups. The neat SPS film demonstrates similar IR spectrum compared to the SPS-C composite films, irrespective of their SPC concentration. The addition of SPC shows insignificant effect on the IR spectrum of SPS films due to the lack of new peaks. This phenomenon manifest that SPC and SPS matrix have similar chemical groups and indicates potential compatibility between the two components. Alternatively, the similarity between the IR spectra of SPS based films before and after SPC reinforcement might exist because both SPS and SPC originated from a single source (sugar palm tree).

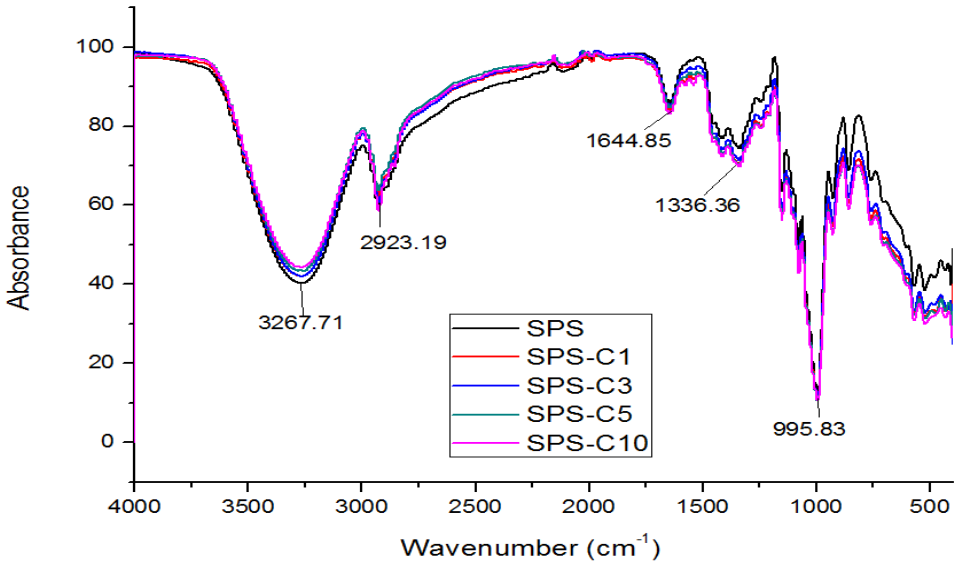
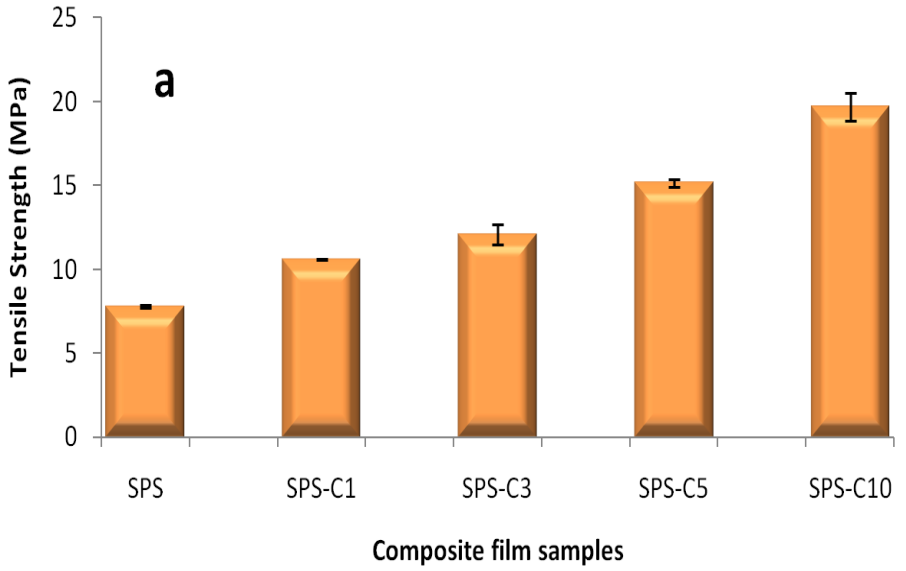


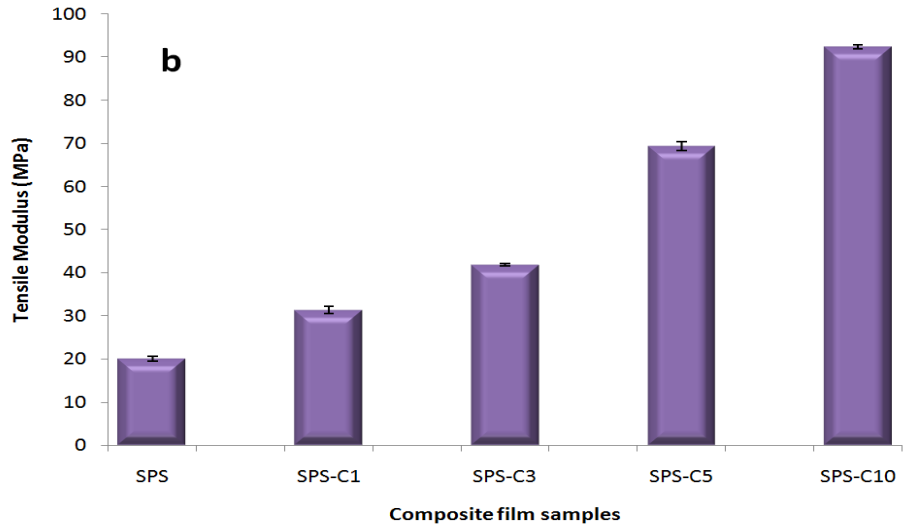
Figure 9.3: IR spectra of neat SPS and SPS-C composite films

9.3.3. Tensile properties

The effect of SPC loading on the tensile strength, tensile modulus and elongation at break of SPS based composite films were determined and the results are presented in Figure 9.4. As expected, it can be notice that the tensile strength and tensile modulus of SPS-C composite films increases as the SPC concentration increased from 1 to 10 wt. %. The tensile strength and tensile modulus of the neat SPS film were 7.79 MPa and 20.11 MPa, respectively. Adding 1 – 10 wt. % SPC reinforcement significantly improved the tensile strength and tensile modulus values of composite films from 10.5 – 19.68 MPa and 31.38 – 92.33 MPa, respectively. Hence, at the maximum SPC loading (10 wt. %) the tensile strength of SPS-C10 improved 60.42 % while the tensile modulus increased 78.22 % higher than that of the neat SPS film. This observed tensile behavior can be attributed to the favorable interaction between SPC

and SPS matrix which facilitate adequate interfacial adhesion owing to their chemical similarities. Similar results were reported by other authors (Dias et al., 2011; Pereda, Amica, Rácz, & Marcovich, 2011). In addition, contrary to the increase in tensile strength and tensile modulus, the elongation at break for the composites films decreased from 40.99 to 32.8 % as SPC concentration increased from 1 to 10 wt. % in the neat SPS films. This marks about 30 % reduction in the elongation at break for SPS-C10 composite film compared to the neat SPS film. The introduction and increase of SPC decrease the molecular mobility of the SPS matrix making the composite materials stiffer. Therefore, SPS-C composite films become more resistant to break, more stiff and less stretchable that the virgin SPS films.





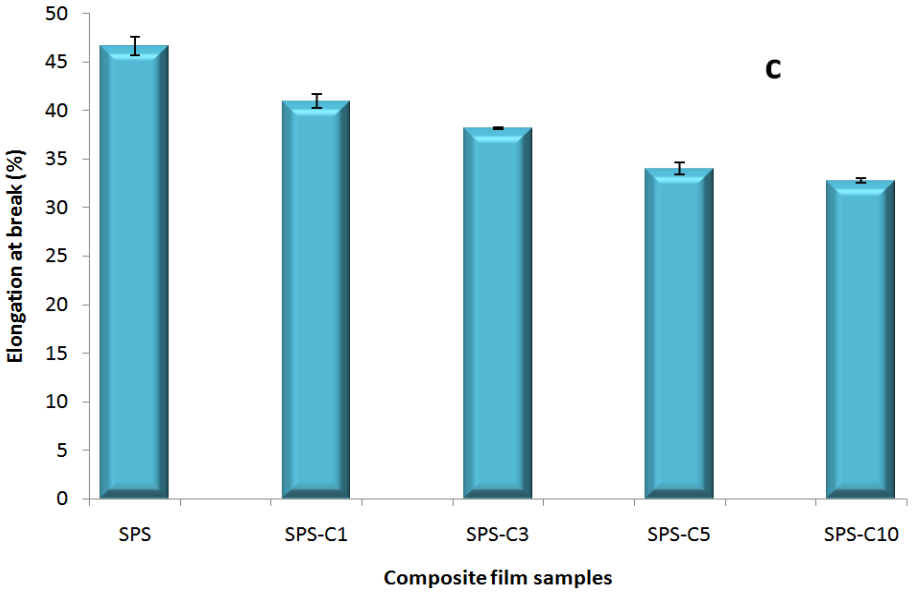


Figure 9.4: Effect of SPC loading on the tensile strength (a), tensile modulus (b) and elongation at break (c) of SPS-C composite films compared to the neat SPS film

9.3.4. Water vapor permeability (WVP)

Films with low WVP are more suitable for food packaging applications to refrain or minimize moisture transfer between the food and the surrounding environment. On this basis, reducing the WVP of SPS films is crucial for their wide application. The WVP of neat SPS and SPS-C composite films are presented in Figure 9.5. It can be seen that SPS film has the highest WVP ($6.373 \times 10^{-10} \times g \cdot s^{-1} \cdot m^{-1} \cdot Pa^{-1}$) due to its high hydrophilic nature. As observed in Figure 9.5, the presence of SPC drastically improves the WVP of the neat SPS film. The addition of 1 wt. % SPC into SPS films decreases their WVP value by 63.53 %. This reduction can be attributed to the tortuous path caused by the dispersed SPC in the starch matrix which hinder or prolong the path for the water molecules to pass through. Increasing the SPC concentration from 1 to 10 wt. % shows slight decrease in the WVP of composite films from $2.324 \times 10^{-10} \times g \cdot s^{-1} \cdot m^{-1} \cdot Pa^{-1}$ to $1.854 \times 10^{-10} \times g \cdot s^{-1} \cdot m^{-1} \cdot Pa^{-1}$. Thus, SPS-C10 displayed 70.91 % improvement in WVP compared to the neat SPS film.

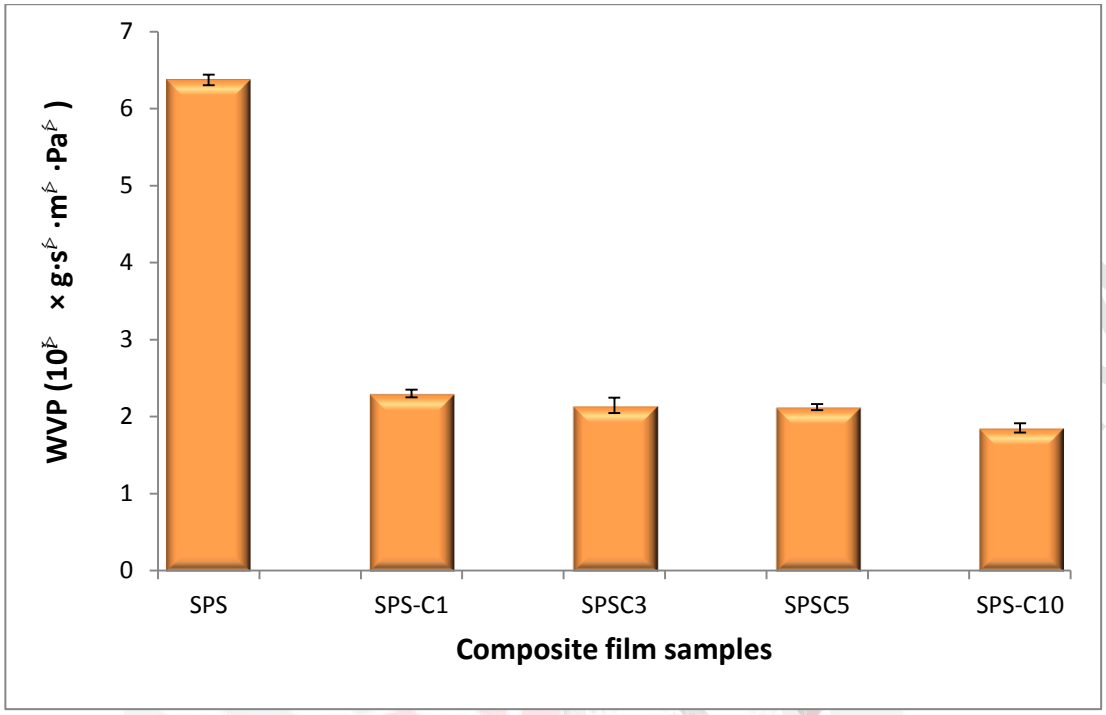


Figure 9.5: Effect of SPC loading on the WVP of SPS-C composite films compared to the neat SPS film

9.3.5. Surface morphology of composite films

Figure 6 shows the FESEM images of the surface morphology of SPS based films with and without SPC. The micrograph of the virgin SPS film manifested a smoother and continuous surface without any trace of starch granular or cracks. Similar observation were reported by Sanyang et al. (2015) and Dias et al. (2011) for neat sugar palm starch and rice flour films, respectively. On the other hand, the addition of 10 % SPC to a virgin SPS film (SPS-C10) display even random distribution of SPC within the SPS matrix without pores or cracks. However, the SPS-C10 composite film surface became rougher with some of the SPC fibers overlapping but no noticeable clusters or agglomerate of SPC. Therefore, the good dispersion of SPC evident shown in Figure 6b is a good indication of strong interfacial adhesion between the two components of the SPS-C10 film. This strong interfacial adhesion translates into its high tensile strength. Our findings concur with the ones reported by Bilbao-Sainz et al. (2011) and Savadekar and Mhaske (2012). In fact, Bilbao-Sainz et al. (2011) reported that cellulose fibers must be well dispersed in the polymeric matrix to enhance the functional properties of the composite.

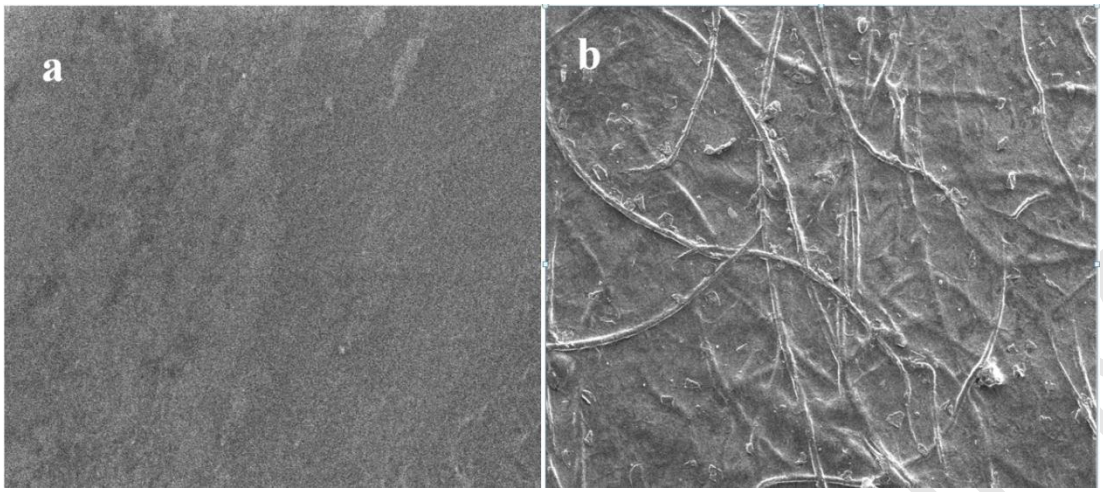


Figure 9.5: FESEM micrographs of neat SPS film (a) and SPS-C10 film (b)

9.4. Conclusion

SPC has been extracted from sugar palm fibers by delignification and mercerization techniques. The effects of SPC loading on the mechanical and water vapor barrier properties of SPS based films were evaluated. Mechanical properties such as tensile strength, tensile modulus and elongation at break as well as water vapor permeability (WVP) of SPS-C composite films were analyzed. The addition of SPC considerably improved the overall mechanical properties and the water vapor barrier of composite films. The FESEM showed adequate random dispersion of SPC in the SPS matrix. This was attributed to the good compatibility between the two components as a result of their chemical similarities. Hence, this study manifests the great potential of SPS-C composite films for packaging applications.

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